

SHIP PRODUCTION COMMITTEE  
FACILITIES AND ENVIRONMENTAL EFFECTS  
SURFACE PREPARATION AND COATINGS  
DESIGN/PRODUCTION INTEGRATION  
HUMAN RESOURCE INNOVATION  
MARINE INDUSTRY STANDARDS  
WELDING  
INDUSTRIAL ENGINEERING  
EDUCATION AND TRAINING

December 1997  
NSRP 0508

# **THE NATIONAL SHIPBUILDING RESEARCH PROGRAM**

## **Document Technologies Available to Clean Brackish Waters to 50 PPT TBT Levels**

U.S. DEPARTMENT OF THE NAVY  
CARDEROCK DIVISION,  
NAVAL SURFACE WARFARE CENTER

in cooperation with  
National Steel and Shipbuilding Company  
San Diego, California

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE <b>DEC 1997</b>		2. REPORT TYPE <b>N/A</b>		3. DATES COVERED <b>-</b>	
4. TITLE AND SUBTITLE <b>The National Shipbuilding Research Program, Document Technologies Available to Clean Brackish Waters to 50 PPT TBT Levels</b>				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Naval Surface Warfare Center CD Code 2230-Design Integration Tower Bldg 192, Room 128 9500 MacArthur Blvd Bethesda, MD 20817-5700</b>				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release, distribution unlimited</b>					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT <b>SAR</b>	18. NUMBER OF PAGES <b>63</b>	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>			

## DISCLAIMER

These reports were prepared as an account of government-sponsored work. Neither the United States, nor the United States Navy, nor any person acting on behalf of the United States Navy (A) makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness or usefulness of the information contained in this report/manual, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or (B) assumes any liabilities with respect to the use of or for damages resulting from the use of any information, apparatus, method, or process disclosed in the report. As used in the above, "Persons acting on behalf of the United States Navy" includes any employee, contractor, or subcontractor to the contractor of the United States Navy to the extent that such employee, contractor, or subcontractor to the contractor prepares, handles, or distributes, or provides access to any information pursuant to his employment or contract or subcontract to the contractor with the United States Navy. ANY POSSIBLE IMPLIED WARRANTIES OF MERCHANTABILITY AND/OR FITNESS FOR PURPOSE ARE SPECIFICALLY DISCLAIMED.

**Document Technologies Available to  
Clean Brackish Waters to 50 PPT TBT  
Levels**

**December 1997**

**Prepared for:**

**National Shipbuilding Research Program  
Panel SP-1**

**Submitted by:**

**Old Dominion University Research  
P.O. Box 6369  
Norfolk, VA 23523**

**N1-96-4  
Subtask 22**

# **APPLIED MARINE RESEARCH LABORATORY**

**College of Sciences  
Old Dominion University  
Norfolk, VA 23529-0456**

## **CENTER FOR ADVANCED SHIP REPAIR AND MAINTENANCE**

**222 E. Main Street  
Norfolk, VA 23510**

### **A REVIEW TO DETERMINE STATE-OF-THE-PRACTICE TREATMENT TECHNOLOGIES FOR REDUCING CONCENTRATIONS OF ORGANO TIN COMPOUNDS IN WASTEWATER**

#### **FINAL REPORT**

Prepared by:

Principal Investigator:	Dr. Alan W. Messing
Project Researcher:	Ms. Lisa M. Ramirez
Project Researcher:	Dr. Thomas Fox

Prepared for:

Mr. Thomas L. Beacham  
Norfolk Shipbuilding & Drydock Corporation (NORSHIPCO)  
750 West Berkeley Ave.  
Norfolk, VA 23523

Submitted by

Old Dominion University Research Foundation  
P.O. Box 6369  
Norfolk, Virginia 23508-0369

AMRL Technical Report No. 3060

December 1997

**A REVIEW TO DETERMINE STATE-OF-THE-PRACTICE TREATMENT TECHNOLOGIES FOR  
REDUCING CONCENTRATIONS OF ORGANO TIN COMPOUNDS IN WASTEWATER**

**TABLE OF CONTENTS**

	<b><u>Page</u></b>
Executive Summary.....	1
Introduction.....	2
Legislative History .....	3
CHAPTER 1 - REVIEW OF PRIMARY MATERIAL	
Literature Review.....	4
U.S. Patent Review .....	6
Survey of Manufacturers and Users of TBT .....	8
CHAPTER 2- DISCUSSION	
Discussion of Practical Alternatives for Removal of TBT from Water.....	10
Technical Approaches Most Likely to Succeed.....	10
Technical Approaches Less Likely to Succeed.....	11
Citations.....	12
Appendix A - Abstracts of Research Concerning Tributyltin in Wastewater and Sewage Sludge.....	14
Appendix B - Annotations of Research Related to Tributyltin .....	21
Appendix C - Personal Communications.....	28
Appendix D - Questionnaire Responses.....	31
Appendix E - Patent Search Results.....	53

# **A Review to Determine State-of-The-Practice Treatment Technologies For Reducing Concentrations of Organotin Compounds in Wastewater**

## **Executive Summary**

The purpose of this study is to identify practical technology that can be used by shipyards to remove tributyltin (TBT) from large volumes of water to levels below 50 parts per trillion. This study is based on: (1) a review of scientific and engineering literature, (2) a review of U.S. Patents, and (3) a survey of manufacturers and users.

TBT based paints are the most popular antifouling paints used on the hulls of the global merchant fleet, and the market share of TBT is still growing despite its banning or partial banning in certain areas. Shipyards generate large volumes of TBT-laden washwater during normal drydock operations.

TBT has been found to be highly toxic in marine environments with observable environmental impacts at levels of parts per trillion. In 1997, after 10 years of study, The United States Environmental Protection Agency (U.S. EPA) proposed a national saltwater aquatic life criteria for TBT of 10 parts-per-trillion (62 CFR 42554, August 7, 1997). After the appropriate comment period, the standard chosen will become the basis for state water quality standards and water discharge permits throughout the U.S.

This study concludes:

1. There is no "off-the-shelf" technology directly applicable to shipyard waste streams that will reduce TBT levels in water below a concentration of 50 parts per trillion.
2. Because TBT is highly attracted to particulates in water, adsorption process may prove be the most effective means to reduce TBT concentration. It is suggested that technology such as Dissolved Air Flootation, and Activated Carbon adsorption are the best candidate technologies.
3. While there are accepted and practical water treatment technologies that may be effective in reducing TBT concentrations in waste streams, these technologies have not been applied to shipyard waste streams. It is recommended that practical trials be conducted as soon as possible.

## Introduction

It is estimated that between 70% and 80% of the global merchant fleet has tributyltin (TBT) antifouling paint applied to their hulls. When these ships are dry-docked, shipyards can generate tens of thousands of gallons of TBT contaminated washwater. For twenty years a substantial global effort has been focused on qualifying the adverse ecological effects of TBT and other organotin compounds in aqueous environments, but very little work has been done to develop practical methods to remove TBT from wastewater streams. At this time U.S. shipyards have no practical guidance on any technology that can be employed to meet regulatory discharge limits. Responding to a written survey question about legislation limiting TBT concentrations in water or wastewater, Arcino Quiero Jr. of Newport News Shipbuilding states: "We are required by our VPDES [Virginia Pollution Discharge Elimination System] permit to submit to the DEQ [Department of Environmental Quality] quarterly progress reports and achieve compliance with final [discharge] limits, **50 ppt**, within four years from the effective date of our permit, June 4, 2000."[sic] This value is based on the current water quality criteria for TBT in Virginia waters. According to the Virginia Code (9VAC25-260-130) "[TBT] in freshwater shall not exceed 0.026 parts per billion ( $\mu\text{g/l}$ ), and the concentration of tributyltin in saltwater shall not exceed 0.001 parts per billion ( $\mu\text{g/l}$ )."

Currently, the reduction of TBT concentrations has been accomplished by limiting or banning products that contain TBT (primarily anti-fouling paints). This control strategy of reducing TBT concentrations by limiting or banning TBT-containing products is a high priority in management guidelines suggested by international, federal and state agencies. The approach of reducing TBT concentrations by reducing the use of products containing this compound does not address the difficulties encountered by facilities that do not manufacture or use TBT-containing products, but come in contact with the substance from outside sources. There is very little published information concerning the treatment of TBT in wastewater.

The problem has become urgent. Two Virginia shipyards have water discharge permits that require compliance with Virginia's standard (50 ppt) within two years. Furthermore, US EPA in August, 1997, issued for comment a draft national standard. The Applied Marine Research Laboratory (AMRL) of Old Dominion University in conjunction with the Center for Advanced Ship Repair and Maintenance (CASRM) instituted a literature search to determine the state-of-the-art technological practices regarding the reduction of TBT concentrations in wastewater. The project has 3 components: (1) a search of scientific and engineering literature; (2) a search of patent literature; and (3) a survey of TBT users and manufacturers of the technology employed in industry. Manufacturers of TBT, industries that incorporate TBT into their products, state and federal regulatory agencies, and Regional Water Control Boards were also contacted by phone. Surveys were sent to shipyards, researchers, and industries to gain information concerning TBT disposal in waste streams. This report summarizes those findings.

After an extensive inquiry, several avenues of exploration that held promise did not yield the expected results. In particular, the Royal New Zealand Navy voluntarily implemented a waste water collection and treatment system of TBT for the effluent from the large dry-dock at the Devonport Base (de Mora, *et al.*, 1995). Inquiries to the naval attaché at the New Zealand Embassy in Washington, D.C., have not produced results in time for inclusion in this report. Also, the International Maritime Organization may be of help in finding suitable technology.



## Legislative History

Tributyltin achieved notoriety during the early 1980s as a result of its use as an active biocide in antifouling paints. It was used as a substitute for organo mercury, arsenic or lead boosters in copper based paints or as the sole biocidal agent. It was once described as the most toxic substance ever deliberately introduced into the aquatic environment and caused damage by leaching from boat hulls and aquaculture cages into the water column (Goldberg, 1986). Particularly high concentrations occurred, therefore, in the vicinities of fish farms, harbors, marinas and other areas of high boat use.

The first evidence of the harmful effects of TBT come from Arcachon Bay on the west coast of France in the mid 1970's (Alziew, 1986). Oyster culture and pleasure boating are traditional activities there, and TBT contamination from boats was linked to high mortalities of oyster larvae and such severe malformations of the shells of adults that they were unmarketable.

Since that time, the adverse environmental effects of TBT have been studied extensively. A search of all TBT studies through 1995 found over 600 scientific papers.

As a result of all the attention, many countries have implemented a variety of laws controlling the release of organotin into the environment. Virtually all of the new regulations are directed toward the use of antifouling paint.

The first regulatory actions were adopted in France in 1982 when the government banned the application of antifouling paints to hulls of most boats shorter than 25 meters (Abel, *et al.*, 1986)

Britain introduced regulations in 1985 controlling the TBT content and release rate in paints. A safe target goal of 20 µg/L was established. In 1987 this target was reduced to 2 µg/L (Vosser, 1987).

In the United States, the United States Environmental Protection Agency (USEPA) commenced a special review of TBT on antifouling in 1986. The Commonwealth of Virginia in 1987 enacted legislation similar to that already in place in Europe (Code of Virginia, Title 3.1). Maryland, California, Michigan and several other states followed suit. In 1988 the U.S. Congress passed the Organotin Act of 1988. It established interim restrictions on painting vessels shorter than 25m (except aluminum) and required paints to have a leach rate of no greater than 4.0 mg/cm<sup>2</sup>/day. It stated that the prohibition could remain in place until a final decision was issued by the administrator of the USEPA (U.S. Public Law, 1988)

In August 1997 the USEPA issued an "Ambient Water Quality Criteria Document for Tributyltin", for comment (US EPA, Federal Register). This document proposes a Final Chronic Value concentration of 0.01 µg/L and a Species Mean Acute Value of 0.61 µg/L.

Also, in 1997, the International Maritime Organization reviewed comments on a proposal to ban the application of TBT world wide. This ban to be effective 10 years after enactment. Action on this proposal is expected in 1998 (IMO, 1997).

## CHAPTER 1 REVIEW OF PRIMARY MATERIAL

### Literature Review (Prepared by AMRL)

Manufacturers of TBT, companies that incorporate TBT into their products, and researchers dispose of waste in one of four ways. Those companies and laboratories that use TBT in research quantities incinerate the hazardous waste components of the TBT waste stream in accordance with 40 CFR 260-263. This method destroys the organic component and renders the residue non-hazardous waste. Other companies transport their waste to US EPA permitted Treatment/Storage/Disposal facilities, also in compliance with 40 CFR 260-263. Many companies that incorporate TBT into their products (i.e., woodstains, paints) do not generate TBT containing hazardous waste. TBT is delivered in drums and is placed in holding vats. The only residual product associated with TBT is the drum in which it is delivered. The drums are triple rinsed in compliance with 40 CFR 260-263 and are, therefore, no longer subject to RCRA waste characterization. They are returned to manufacturer or are transported to a drum disposal unit. The rinsate is placed into the holding tank and incorporated into the product.

The major manufacturer of TBT in the United States, Elf-Atochem, recovers all waste generated. Solid and aqueous waste is transported to a tin recovery unit where it is incinerated at high temperatures to destroy any organic components. The resulting slag is sent to a smelting facility and is purified into tin ingots that are returned to the plant to be used in synthesizing more TBT. Another manufacturer located in Germany, Witco Corp., filters its waste and applies several separation processes. The resulting sludge is dried and placed in an approved landfill.

Numerous studies (Laughlin, *et al.*, 1986; Maguire and Tkacz, 1985; Randall and Weber, 1986) have demonstrated that TBT adsorbs to particulate material. This material can be organic or inorganic in nature. Monitoring conducted at a wastewater treatment plant in Zurich, Switzerland, indicated that a large portion of organotin species, including TBT, was removed after the primary clarifying treatment. Analysis indicated that 75% of the TBT was removed and had been transferred to the remaining sewage sludge (Fent, 1996). Initial concentrations of TBT were between 64 and 217 ppt. Concentrations in the secondary effluent ranged from 7-47 ppt. After the secondary sedimentation treatment and aerobic treatment, 90% of the initial TBT concentration was removed from the wastewater. An additional filtration resulted in a 98% removal of the compound. Concentration ranges in the effluent were <1 - 17 ppt. This plant is noted to be more efficient than most treatment facilities in Switzerland.

The Water Resources Division in the City of Livermore, California, monitors for TBT in their waste stream. They have a unique situation in that they are not near a coastal area and the TBT contamination originates from inland areas. Conclusions drawn by their personnel suggest that TBT is originating from water cooling towers, but this has not been confirmed. Procedures for treating wastewater at the Livermore facility start with the addition of iron (II) chloride to remove sulfides and to promote settling. Activated sludge is added and a secondary clarification step follows. Caustic in the form of sodium hydroxide is added to adjust the pH and then sodium hypochlorite is added as a disinfecting agent. Data seems to indicate that wastewater treatment protocols at this facility reduce TBT by 90% or more (Touray, personal communication). However, there is a considerable lag time between influent and effluent sampling and the residence time of the sewage was not stated. Therefore, the reduced concentration of TBT in the effluent may not directly correlate to the initial influent value.

If current wastewater technology proves useful in reducing TBT to acceptable levels by partitioning the compound to the solid phase, the resulting sludge may be a potential source of contamination. Sludge is often dumped at sea and it is also used as a fertilizer. If TBT is present in fertilizer, it may be transferred to soils. At sea, resuspension may occur and TBT may again become a contaminant to aquatic life (Page, 1996).

Sediment samples were collected near a shipyard located on the Fore River near South Portland, Maine, and analyzed for TBT (Page, 1996). Concentrations in the surface sediments ranged from 24-12,400 ng/g on a dry weight basis. Subsequent elutriate analysis determined that TBT was released into the water. The concentration was 0.14% of the total TBT in the sediment sample, suggesting that TBT is released slowly into the water. Even at a slow release rate, there is the potential for future contamination due to the fact that TBT contained in paint chips would be resistant to biodegradation and persist in the sediment. Also, deposit feeders could directly ingest TBT by feeding.

Degradation experiments have been conducted on sewage sludge under both aerobic and anaerobic conditions. (Fent, *et al.*, 1991). Calculated half lives of TBT in water using radio-labeled TBT are approximately 6-7 days (Seligman, *et al.*, 1988). The half life of TBT in the surface sediment is approximately 4-6 months (Stang, *et al.*, 1992). The degradation rates of TBT may be due to the high availability of nutrients in sewage sludge. The nutrients may be a preferred source of carbon for microbes as opposed to the carbon contained in TBT.

TBT degrades to dibutyltin (DBT) and monobutyltin (MBT) and eventually to tin ion. These compounds are less toxic to marine life than TBT. Fungal cultures and freshwater green alga demonstrate the ability to debutylate TBT to DBT and MBT. Diatoms and dinoflagellates also debutylate TBT. While degradation depends upon temperature and the presence of microorganisms, the microorganisms that biodegrade TBT may not be able to survive if the concentration of TBT is too high. Several papers describe microbial biofilms that accumulate TBT without subsequent degradation. No evidence has been found that these microbial methods have been used on a large scale for waste stream treatment.

## **U.S. Patent Review (Prepared by CASRM)**

A search of the U.S. Patent data base has been conducted to identify proprietary technology that can remove tributyltin or organotin, from aqueous streams to purity levels of <50 parts per trillion. The search found no turn-key technology that can accomplish this task.

The search was then widened to determine proprietary technology which can remove organic pollutants from aqueous streams to levels of parts per billion. This search produced a number of patents based on different technical approaches.

### *1. Resin Beds*

A wide variety of cationic, anionic and non polar resins have been employed to purify water. Non-polar resins are effective for the removal of a wide range of organic pollutants.

- U.S. Patent 3,531,463 describes a process to remove phenols and chlorinated hydrocarbons contained in the effluent of a bleached Kraft pulp mill.

While the class of non-polar ion exchange resins have been found to absorb a wide range of organic pollutants, U.S. Patent 5,236,594 describes the benefits of using non-ionic polymeric resins, since these can be regenerated using solvents in which the pollutants are soluble. The preferred resins are products such as:

AMBERLIGHT ®, XAD  
Duolite ®,  
Dialon ®,

Rohm & Haas, Philadelphia, PA  
Chemical Process Co, Redwood, CA  
Mitsubishi Chemical Co, Tokyo, Japan

Water purity levels to 0.1 ppb (100 ppt) are claimed

U.S. Patent 3,853,758 describes the use of this type of resin to remove toxic organic pollutants from the effluent of a dye manufacturing plant. For best results contact times of 2-10 minutes are required. After treatment, pollutants can be extracted from the resin by mixing with solvents in ratio 1 volume of resin: 3 volumes solvent. Solvents can be methanol, acetone, dichloromethane, chloroform, diethyl ether and ethyl acetate.

### *2. Activated Carbon*

Effluent treatment using activated carbon has been found to remove a wide range of organic pollutants from water. A search using key words "activated carbon" and "water purification" revealed in excess of 400 patents issued since 1973. Activated carbon is not selective and removes most organic compounds from water. It cannot be easily regenerated and spent carbon must be disposed by incineration or in an appropriate land fill.

U.S. Patent 5,399,263 describes a water purifier for supplying high purity water with a low organic carbon content. The purifier consists of a multibed purification cartridge having several layers of activated carbon and both cationic and anionic ion exchanger resins. It is claimed that water with a total organic carbon contents of up to 100 ppb (100,000 ppt) is produced.

U.S. Patent 4,007,116 describes a process for purification of wastewaters using activated carbon in a moving fluidized bed arrangement. Granular activated carbon is moved in through the bed in counterflow to the water stream, so as to continuously introduce fresh activated carbon particles at the top of the bed to compensate for using carbon withdrawn at the bottom. Organic carbon contents of 1 ppb (1000 ppt) are claimed.

Activated carbon can be manufactured in a number of different ways and in different forms. We have identified 381 U.S. Patents issued since 1973 describing different processes of preparation, manufacture, and method of use for this product.

### 3. *Ultraviolet Light*

Ultraviolet light has been used to remove organic compounds, and in some cases microbes, from water. The mechanism for removal of organic pollutants is the partial breakdown of the organic molecule by UV and subsequent removal of the disassociation products by some other means.

U.S. Patent 5,302,356 discloses an ultrapure water treatment system comprising a 185 nm UV light source in conjunction with a catalytic filter made of a polymeric porous material with a photoactive catalytic coating. The UV light, catalyst and air act to convert organic contaminants to carbon dioxide.

U.S. Patent 5,061,374 describes a process where-by water is treated in a succession of water treatment steps comprising: mineral filter, mixed ion exchange resin bed, UV light source, a reverse osmosis stage and fine ultrafiltration stage. Final water purity is claimed to be 1 ppb (1,000 ppt).

### 4. *Ultrafiltration*

Many organic contaminants including TBT are attracted to particulates in water. The principle behind ultrafiltration systems is to remove the contaminants by removing the particulates from the water.

Several patents employ ultrafiltration as the final stage of a water purification sequence. U.S. Patents 5,376,281 and 5,302,356 both describe the use of ultrafiltration in conjunction with ultraviolet light.

### 5. *Biological Degradation*

Many industrial effluent streams are treated successfully by microbial degradation.

U.S. Patent 5,653,883 describes a method of removing organic contaminants from water by microbial degradation in a stirred tank system having a powdered or granular media for biofilm support.

Biodegradation will not take place if the pollutant concentration is so high as to poison the microbes. U.S. Patent 5,653,883.

## **Survey of Manufacturers and Users of TBT**

Approximately 150 questionnaires were mailed to several research facilities and laboratories, a manufacturer of TBT, and industries that either incorporated TBT into their products or came in contact with TBT containing products. Sixteen questionnaires were returned. Researchers and laboratories comprise nine of the respondents and industries comprise the remaining seven (see Appendix D).

The only company that monitored for TBT is the manufacturer, Elf-Atochem. Generated waste is sent to a tin recovery unit. All solid and aqueous waste is incinerated at high temperatures, which destroys the organic portion. The resulting slag is delivered to a smelting facility and the tin is recovered as purified ingots to be used in further TBT synthesis.

Companies that incorporate TBT into their products do not monitor for TBT because they do not generate a wastewater stream. Washdowns from TBT holding tanks and rinses from TBT drums are incorporated into the product. Mr. Algimantas Pliodzinskas, the Health and Safety Coordinator at Hempel Coatings (USA), Inc., a marine paint manufacturer, states that “any residue which cannot be utilized in their product is sent for disposal through fuel blending for cement kilns. All TBT containing paint products or raw materials are in a combustible form suitable for fuels blending.”

None of the respondents from companies that incorporate TBT into their product were aware of any legislation in their respective regions that would regulate TBT discharge. Mr. Pliodzinskas stated that organotins are “by definition pesticides and are to be disposed of in accordance with federal, state and local regulations. RCRA regulations do not specifically list tin or TBTs as specific hazardous wastes.”

Most industries (primarily shipyards) that come in contact with products containing TBT are required to monitor for the compound. TBT monitoring is one of the requirements of the National Pollutant Discharge Elimination System (NPDES) permit. National Steel and Shipbuilding Company in San Diego, CA, currently monitors for TBT in the water column surrounding the facility, but not in its own discharge. A discharge of TBT can only occur at pier side at their establishment. Once their NPDES permit is renewed, however, TBT in the shipyard discharge will be monitored as well. This firm does not use any paints containing TBT unless a customer specifically requests it.

To reduce possible TBT contamination when applying TBT-containing paints, Halter Marine Group, Inc. places plastic sheeting on the ground underneath the area to be painted. The plastic is moved from section to section to reduce the quantity of plastic used. This material is analyzed and disposed as a hazardous waste if necessary. Any sludges or solids such as paint suits, brushes, etc. are disposed in a similar fashion if found to be contaminated. When TBT-containing coatings are removed from vessels, the material is contained via “environmental screens” with a shade factor of 90% or more. These screens reduce off-site particulate migration. If the vessel is in dry-dock, “the screens and a temporary steel birm [sic] or wall of 12-18 inches is placed in areas to block any residual runoff.” (Appendix C) Norfolk Shipbuilding and Drydock Corporation (NORSHIPCO) has recently employed carbon-bed technology, but TBT concentrations in wastewater after treatment were 2 ppb; this concentration does not meet the proposed 50 ppt regulation. Still another facility manages its waste according to RCRA waste disposal guidelines.

A feasibility study was conducted by U.S. Filter for Newport News Shipbuilding with guidance from Rohm & Haas and the College of William and Mary Virginia Institute of Marine Sciences. A series of resins was developed for the removal of copper in the effluent, but cost limitations did not allow further study to determine the efficiency of TBT removal.

There are several opinions concerning minimizing the hazards of TBT. One respondent wrote only that Best Management Practices need to be instituted. Suggestions from other respondents include entraining the wastewater and treating it, but details were omitted, and finding alternative sources of anti-foulants. It is understood that new anti-foulants might not be as effective as TBT, but the toxicity to the environment would be less. One shipyard representative stated that if a satisfactory solution for controlling TBT is determined, the rest of the world must adhere to these policies. If not, then contamination would persist despite the efforts to minimize the hazard TBT represents to aquatic life.

Research facilities that responded to the survey monitor for TBT at their respective laboratories or for clients, but do so for research purposes and not for compliance with any regulations. Each laboratory monitors in a slightly different fashion. Some laboratories directly sample and chemically analyze aqueous waste for clients or at their own facility. Others observe the emergence of imposex in biota as a biomarker for the presence of TBT in local coastal waters. Waste from these laboratories is quite small and is either incinerated or sent to a waste handling facility. Researchers have several suggestions for reducing TBT concentrations in water that range from containing initial waste and disposing of it at high temperatures, filtering contaminated water through an organic phase to which TBT will bind, or using biodegradation and biosorption techniques. NuTECH Enterprises, Inc., a waste disposal unit in Oceanside, California, has had success in reducing concentrations of other organometallic substances by using biodegradable quaternary surfactants. This company is willing to conduct experiments to determine if this technology would be suitable for removal of TBT.

Most of the respondents do not know of any legislation enacted or pending that limits TBT concentrations in water. The exceptions are those respondents from Virginia and the United Kingdom (UK). The UK has an environmental quality standard of 2-3 ng/L in seawater - far more stringent than any standard in the U.S. at this time. Opinions on minimizing the hazard posed by TBT vary from banning the substance entirely, enforcing strict containment procedures by employing closed systems in dry docks, developing less toxic alternatives, to conducting a cost/benefit analysis of the use of TBT versus the impact of TBT on marine ecosystems.

## **CHAPTER 2 - DISCUSSION**

### **(Prepared by CASRM)**

#### **Discussion of Practical Alternatives for Removal of TBT from Water**

There is no "off-the-shelf technology" that can be directly used by shipyards to achieve TBT discharge concentrations of <50 ppt.

Due to the very low volatility of TBT compounds, significantly lower than that of water, air stripping is not expected to be of value for removal of TBT from water.

Manufacturers of TBT use incineration to destroy TBT or recycle the TBT in waste streams into new product. These approaches are impractical in shipyards where TBT is dissolved in tens or hundreds of thousands of gallons of wash-water.

Reduction of aqueous TBT concentrations by sewage treatment has been demonstrated at a number of facilities around the world. Adsorption of TBT onto activated sewage sludge is significant. Typical results show influent TBT concentrations of >200 ppt and effluent concentrations of 50-100 ppt. However, one sewage facility in Zurich, which employed an extra treatment step, achieved an effluent concentration of 2 ppt (Fent, 1996). Shipyard effluents can contain >50,000 ppt TBT (Personal Communication with Tom Beacham from NORSHIPCO). This level is sufficiently toxic to suppress all microbial activity in activated sewage sludge (Müller, *et al.*, 1989).

Other technologies may be more directly applicable to shipyards than the technology used in water treatment facilities. The next section describes several approaches that may be more applicable to the removal of TBT from shipyard waste streams.

#### **Technical Approaches Most Likely to Succeed**

##### *1. Dissolved Air Flootation (DAF)*

TBT appears to be highly attracted to particulates in the water. Estimates of the water-solid coefficient range from 1,000 - 10,000 on a weight basis. For instance, Maguire *et al.* (1985) found a partition coefficient of  $2180 \pm 350$  for TBT in water and sediment of Toronto harbor.

A Dissolved Air Flootation system can take advantage of this phenomenon to reduce TBT concentration in water by, perhaps, 1,000 times.

Control of pH may be important. Müller *et al.* (1989) showed solubility of TBT in water was minimum at a pH of 6.

Absorption processes may be able to reduce TBT levels to less than 50 ppt. In one sewage plant in Switzerland, TBT levels in water were reduced from 181 ppt to 9 ppt mainly by sedimentation in the primary classifier and subsequent treatment steps (Fent 1996).



## 2. *Solid Phase Extraction*

Activated carbon has been used to remove a wide range of organic pollutants from water streams including organo lead compounds. Maximum pollutant removal may be achieved using a counterflow fluidized bed arrangement as described in U.S. Patent 4,007,116, which demonstrated organic carbon levels of less than 1 ppb.

Alternative non-ionic polymeric resin beds may be effective. Products such as AMBERLIGHT, XAD from Rohm and HAAS have been reported to achieve 0.1 ppb with very toxic organic pollutants in the effluent of bleach kraft pulp mills and dye manufacturing plants.

### **Technical Approaches Less Likely to Succeed**

#### 1. *Microbial Degradation*

Microbial degradation appears to be possible in water if the concentration of TBT is not too high, but the process is slow. Seligman *et al.* (1986) found a half life of TBT of 6-7 days, when the concentration was 500 ppt, but no degradation at all took place at TBT concentration of 7400 ppt.

Microbial degradation is dependent on temperature. Several reports indicate that little or no microbial degradation occurs in winter.

#### 2. *Ultraviolet Light*

There is some disagreement about the effects of UV light on TBT. Seligman *et al.* (1986) demonstrated that degradation of TBT in the water of San Diego Bay was caused by microbial action and not due to ultra violet light. However, there are laboratory studies which show that UV degradation does occur half lives in the range 0.6 days to 18 days.

## CITATIONS

- Abel, R., *et al.*. In *Proceedings Oceans '86 Organotin Symposium* (1986) vol. 4. IEEE: Washington D.C., 1314-23.
- Alziew, C. In *Proceedings Oceans '86 Organotin Symposium* (1986) vol. 4. IEEE: Washington D.C., 1130-34.
- Code of Virginia (1987). Title 3.1, Chap 14, Article 5, Sections 3.1-249.22 - 3.1-249.26.
- de Mora, S.J., C. Stewart, D. Phillips. *Marine Pollution Bulletin* (1995) 30:1, 50-57. Sources and Rate of Degradation of Tri(n-butyl)tin in Marine Sediments Near Auckland, New Zealand.
- Fent, Karl, *et al.* *Marine Environmental Research* (1991) 32, 223-231. Fate of Tributyltin in Sewage Sludge Treatment.
- Fent, Karl. *The Science of the Total Environment* (1996) 185, 151-159. Organotin Compounds in Municipal Wastewater and Sewage Sludge: Contamination, Fate in treatment process and ecotoxicological Consequences.
- Fent, Karl and Müller, Markus D. *Environmental Science and Technology* (1991) 25, 489-493. Occurrence of Organotins in Municipal Wastewater and Sewage Sludge and Behavior in a Treatment Plant
- Goldberg, E.D. *Environment* (1986) 28, 17-44. TBT an Environmental Dilemma.
- International Maritime Organization (IMO). Marine Environmental Protection Committee (MEPC) of the IMO. MEPC 40 Draft Report, Agenda Item 11 (Antifoulants). London, England, September, 1997.
- Laughlin, Roy B., Jr., Harold E. Guard, William M. Coleman, III. *Environmental Science and Technology* (1986) 20:2, 201-204. Tributyltin in Seawater: Speciation and Octanol-Water Partition Coefficient.
- Maguire, R. James and Tkacz, Richard. *Journal of Agriculture and Food Chemistry* (1985) 33, 947-953. Degradation of the Tri-n-butyltin Species in Water and Sediment from Toronto Harbor.
- Müller, Markus D., Lara Renberg, Gerd Rippen. *Chemosphere* (1989) 18:9/10, 2015-2042. Tributyltin in the Environment - Sources, Fate and Determination: An Assessment of Present Status and Research Needs.
- Page, D.S., C.C. Ozbal, M.E. Lanphear. *Environmental Pollution* (1996) 91:2, 237-243. Concentration of Butyltin Species in Sediments Associated with Shipyard Activity.
- Randall, Louise and Weber, James H. *The Science of the Total Environment* (1986) 57, 191-203. Adsorptive Behavior of Butyltin Compounds Under Simulated Estuarine Conditions.
- Seligman, Peter F., Aldis O. Valkirs, Peter M. Stang, Richard F. Lee. *Marine Pollution Bulletin* (1988) 19:10, 531-534. Evidence for Rapid Degradation of Tributyltin in a Marina.

Stang, Peter M., Richard F. Lee, Peter F. Seligman. *Environmental Science and Technology*, (1992) 26:1382-1387. Evidence for Rapid, Nonbiological Degradation of Tributyltin Compound in Autoclaved and Heat-Related Fine-Grained Sediments.

U.S. Public Law 100-333; 102 Stat. 605; June 16, 1988. Organotin Antifouling Paint Control Act.

U.S. EPA Code of Federal Register, Vol 62 No. 152, p. 42554, August 7, 1997. Notice of Ambient Water Quality Criteria for Tributyltin (TBT) and Request for Comments.

Vosser, J.L. *Antifoulings Paints News Release* (1987). Department of Environment, London, England.

## **Appendix A**

### **Abstracts of Research Concerning Tributyltin in Wastewater and Sewage Sludge**

Argaman, Y., C.E. Hucks, S.E. Shelby, Jr. *Water Research* (1984) 18:5, 535-542. The Effect of Organotin on the Activated Sludge Process.

Organotin compounds which find increasing use in marine antifouling paints may be present in the discharge from dry dock operations. This investigation was aimed at determining the effect of such wastewater when discharged to a municipal activated sludge treatment plant. Experiments were conducted using a Warburg respirometer and continuous flow bench-scale activated sludge system. The results showed that unacclimated biological cultures can be inhibited by tributyl tin oxide (TBTO<sup>TM</sup>) concentrations as low as 25  $\mu\text{g l}^{-1}$ . However, TBTO doses of over 8000  $\mu\text{g l}^{-1}$  can be tolerated by a well acclimated culture. Continuous loading of up to 1000  $\mu\text{g l}^{-1}$  TBTO had no effect on organic removal in activated sludge systems. However, an adverse effect on sludge settleability was noticed at 100  $\mu\text{g l}^{-1}$  TBTO. Shock loadings of 500 and 1000  $\mu\text{g l}^{-1}$  TBTO had no effect on soluble organic removal but resulted in impaired settling and higher effluent suspended solids. The  $\text{LC}_{50}$  of TBTO to the fathead minnow was estimated at 45-200  $\mu\text{g l}^{-1}$ . The toxicity was reduced considerably by activated sludge treatment.

Chau, Y.K., Shuzhen Zhang, R. James Maguire. *The Science of the Total Environment* (1992) 121, 271-281. Occurrence of Butyltin Species in Sewage and Sludge in Canada.

Samples of sewage treatment influent, effluent and sludges collected monthly from five Canadian cities over the period from July 1990 to January 1991 were analysed for butyltin and octyltin species. Monobutyltin was found in all influent samples, but dibutyltin and tributyltin were found only infrequently, and octyltin species were not found at all. In the case of monobutyltin, there was significant reduction in its concentration by degradation and adsorption to sludge during passage through the sewage treatment plant. The average reduction was 40%. The monobutyltin found in the effluent likely came from its use as a poly (vinyl chloride) stabilizer, and from the degradation of tributyltin, which is used as a slimicide. No butyltin or octyltin species was found in five landfill samples in southern Ontario during the same period.

Elimination of monobutyltin in the sewage treatment plant process did not appear to be as efficient as was observed in the Zurich sewage treatment plant. The average reduction was 40% with a range of 19-75%. High concentrations of butyltins in sludge were found. Residual concentrations of monobutyltin at the  $\mu\text{g/L}$  level in the effluent will probably not pose a hazard to aquatic organisms since the effluent will eventually be greatly diluted and toxicity of monobutyltin to aquatic organisms has only been observed at much higher concentrations ( $\text{mg/L}$ ).

Donard, O.F.X., Ph. Quevauviller, A. Bruchet. *Water Research* (1993) 27:6, 1085-1089. Tin and Organotin speciation during Wastewater and Sludge Treatment Processes.

The speciation of inorganic tin and organotin compounds is studied in raw water samples and in filtered water samples collected along the main steps of the wastewater treatment plant of Bordeaux City (France). Analyses are performed by hydride generation, cryogenic trapping, chromatographic separation and detection by atomic absorption spectrometry. Results show that dissolved inorganic methylated tin (mono-, di-, trialkylated forms) and butyltin compounds (mono- and dialkylated forms) occur at all stages of the water treatment process. Butyltins were found at low concentration levels which tends to show that the weathering of PVC is a minor phenomenon. High methyltin contents were however found which illustrate the high methylation rate in sewage water; a general removal trend from the water is observed for inorganic and methyl-tin species both in raw water and filtered water samples. Volatilization of tin compounds is observed in the anaerobic fermentation steps of the activated sludge. Possible pathways for transformation of tin (methylation, volatilization) during the wastewater treatment are discussed.

The efficiency of tin and organotin removal is directly regulated by their adsorption capacities. Tin can be methylated and methyl- and butyltins can display different adsorption behaviours depending upon the size of the alkyl group.

Fent, Karl. *Marine Environmental Research* (1989) 28, 477-83. Organotin Speciation in Municipal Wastewater and Sewage Sludge: Ecotoxicological Consequences.

Direct entry of the extremely toxic tributyltin (TBT) into the aquatic environment is primarily due to its use in antifouling paint biocides on ships. Growing concern has been raised regarding their impact on aquatic organisms since TBT is among the most toxic pollutants for aquatic ecosystems. Accurate and precise quantitative methods are needed for speciation of organotins in complex matrixes like wastewater, sludge, sediments and biological materials. While contamination of water and sediments is known to a certain extent in a number of marines, organotin species and contamination in municipal wastewater and sewage sludge are largely unknown. In this study, organotins were determined by extraction, ethylation by a Grignard reaction and analysis by gas chromatography with flame photometric detection (GC-FPD). Limit of detection was 1-10 ng/litre for each organotin species. For higher accuracy, four separate internal standards with different degrees of alkylation were used. IN raw wastewater mean concentrations on 3 days were (as ions): 199 ng/litre of monobutyltin (MBT), 164 ng/litre of dibutyltin (DBT), and 173 ng/litre of TBT (total 536 ng/litre). Mono-, di-, and triphenyltin, tricyclohexyltin and dioctyltin were not detected. About 90% of each butyltin species were associated with particles, and thus removed to a large extent by sedimentation in the first step of treatment plant. In sewage sludge, organotins were accumulated to relatively high concentrations. In one sample of digested sludge the following concentrations were determined: MBT 0.6 mg/kg, DBT 1.2 mg/kg and TBT 1.1 mg/kg (dry wt). It is concluded that untreated wastewater could give rise to pollution of aquatic systems. As sludge is used for fertilizer in agriculture, organotins are transferred to soils. In addition, since sludge is dumped at sea in large amounts, a mainly unrecognized source of TBT in the marine environment is identified.

The high concentration of TBT in sludges was not substantially changed even after 35 days of anaerobic degradation. MBT and DBT (less toxic to biota) probably originate from manufacture of polyvinyl chloride (PVC) and other plastics and might also leach from PVC. TBT probably originates from its use in material protection (fungicidal wood and textile preservation) disinfectants and from cooling water towers. Untreated municipal wastewater is therefore a source of organotin contamination in aquatic ecosystems.

Fent, Karl. *The Science of the Total Environment* (1996) 185, 151-159. Organotin Compounds in Municipal Wastewater and Sewage Sludge: Contamination, Fate in treatment process and ecotoxicological Consequences.

Organotin compounds find various applications in industry and agriculture, which may lead to contamination of municipal wastewater and sewage sludge. Here, an overview on the contamination of these media is given, and the behavior of organotins in the treatment process is described. In raw municipal wastewater of the city of Zürich, Switzerland, mono-(MBT), di-(DBT) and tributyltin (TBT) were detected in the range of 140-560, 130-1030, and 60-220 ng/l, respectively. These compounds were primarily associated with suspended particulates, and transferred from wastewater to the sludge in the primary clarifier of the treatment plant. Both aerobic and anaerobic degradation were found to be insignificant. This has also been shown by a laboratory-scale sludge treatment system. After secondary and tertiary treatment, organotin concentrations were in the range of < 1-17 ng/l in the effluent of the plant. In digested sludge, concentrations of MBT, DBT, and TBT were in the range of 0.3-0.8, 0.5-1.0 and 0.3-1.3 mg/kg (dry weight), respectively, in 1988-1990. A survey in 1995 in 25 treatment plants showed a similar contamination pattern with averages  $\pm$

S.E.M. of  $0.5 \pm 0.2$  mg/kg MBT,  $1.5 \pm 0.5$  mg/kg DBT and  $1.1 \pm 0.4$  mg/kg TBT. In seven sludges, phenyltins were found with averages of  $0.1 \pm 0.04$  mg/kg, monophenyltin,  $0.1 \pm 0.06$  mg/kg diphenyltin and  $0.5 \pm 0.2$  mg/kg triphenyltin. The ecotoxicological consequences of organotin-polluted wastewater and sludge should be regarded concerning both the discharge of wastewaters into aquatic systems and the use of digested sludge as a soil amendment. Adverse effects on the most sensitive aquatic biota (gastropods) in receiving waters were shown at the concentrations found in plant effluents. The ecotoxicological implications of sludge derived organotin pollution on soils are not well understood, but bioaccumulation of these compounds in the terrestrial food web may occur.

TBT in wastewater is primarily associated with suspended solids. In this study approximately 83-92% of TBT was associated with solid material. Approximately 75% of butyltins were removed by sedimentation in the primary clarifier. In the effluent, butyltins range from  $< 1$ -17 ng/L. Combined treatment steps eliminated 98% of the influent concentration. Aerobic and anaerobic degradation were insignificant compared to the removal of TBT by sedimentation. In one case 73% of the butyltin load was eliminated by sedimentation and biodegradation by activated sludge had net reduction of 8%. Primary and secondary sedimentation and aerobic treatment resulted in a 90% butyltin reduction. An additional filtration step led to a 98% overall elimination of butyltins. TBT degradation in sewage sludge was low (max 30%). Sorption of TBT onto particulate organic sludge and the abundance of nutrients available to microorganisms in sludge results in a reduction of the bioavailable fraction of TBT to the microorganisms. This may result in a less preferred assimilation of carbon from the degradation of TBT.

Fent, Karl, Judith Hunn, Dea Renggli, Hansruedi Siegrist. *Marine Environmental Research* (1991) 32, 223-231. Fate of Tributyltin in Sewage Sludge Treatment.

We have shown that municipal wastewater and sewage sludge are contaminated by organotins. Here, we investigate the behaviour and fate of tributyltin (TBT) in laboratory-scale sewage sludge treatment at various conditions including both aerobic and anaerobic, and mesophilic and thermophilic. Organotins were determined by capillary GC-FPD. Fresh raw sewage sludge was stored in a tank that was connected to five chemostats maintained at different conditions. Raw sludge contained TBT, dibutyltin (DBT) and monobutyltin (MBT) residues in the range of 0.28 to 0.83 mg/kg (dry weight). The volumetric TBT concentration was 10.5 ug/litre in the influent, and ranged from 7.4 to 8.3 ug/litre in the effluent of the different chemostats. In the anaerobic mesophilic treatment, concentrations of TBT did not decrease with increasing sludge residence time, DBT increased and MBT showed no clear trend. The DBT increase is suggested to be due to leaching from the PVC walls of the chemostats, and not to degradation of TBT alone. The TBT reduction did not show significant differences between the mesophilic and thermophilic anaerobic fermentors. These findings indicate that the degradation of TBT during sludge treatment is only low under all conditions tested.

Aerobic degradation of TBT has been demonstrated in the water column, with degradation rates varying according to conditions, and half-lives in the range of 6 days to two weeks. Degradation was slow in sediments with half-lives of several months. Degradation of TBTO was observed only during aerobic conditions in the presence of a suitable carbon source. Recently TBTO was shown to degrade aerobically and anaerobically in a mixed bacterial culture from activated sludge in fermentors. While degradation does occur, it is minimal. A reduction in DBT concentration was observed in the aerobic thermophilic treatment only. DBT concentrations increased under anaerobic mesophilic conditions and concentration increases cannot be explained by mass balance. There is a possibility that DBT concentration increased due to leaching from the PVC walls of the chemostats. This is substantiated by the fact that the DBT increase was not observed in the chemostat composed of glass. The low degradation rates of TBT in general may be due to the high availability of nutrients in sewage sludge. This may be a preferred source of carbon rather than TBT.

Fent, Karl and Müller, Markus D. *Environmental Science and Technology* (1991) 25, 489-493. Occurrence of Organotins in Municipal Wastewater and Sewage Sludge and Behavior in a Treatment Plant

The behavior of selected organotin species in a wastewater treatment plant in Zurich, Switzerland, was studied. In untreated wastewater, monobutyltin (MBT), dibutyltin (DBT) and tributyltin (TBT) were detected in the range of 136-564, 127-1026, and 64-217 ng/L, respectively, of which 81-92% were associated with suspended solids. During treatment, the fraction of organotin in the particulate phase decreased with decreasing suspended solids concentration. All organotin species monitored were found to be efficiently in the primary clarifier. In the secondary effluent, levels of different organotins were in the range of 7-47 ng/L. These compounds were transferred into sewage sludge, indicating that the most important process for the elimination of organotins was adsorption into sludge. Residues of MBT, DBT, and TBT in digested sludges were in the range of 0.10-0.97, 0.41-1.24, and 0.28-1.51 mg/kg (dry weight), respectively.

MBT, DBT and TBT were detected in both the dissolved and particulate phases of raw wastewater. In raw wastewater daily variation was greater for DBT and butyltin tin species were primarily associated with suspended solids. In untreated wastewater with highest suspended solids concentration, the proportion of particulate-associated organotins was highest. The partitioning in wastewater between dissolved and particulate-associated organotins was different from the situation observed in the water column of seawater, where generally less than 5% of the total TBT was found in particulate fraction. However, much lower suspended solids concentrations occurred in seawater as compared to wastewater.

Concentrations of butyltins in raw sewage sludge did not differ much when compared to digested sewage sludge (35 days anaerobic digestion). In the digestion supernatant the concentrations of organotins was predominantly associated with particulates (84% in particulate fraction). Concentrations of butyltins in the excess activated sludge that is produced in the secondary and recycled into primary clarifier indicate that the butyltin reduction observed in the secondary effluent was partly due to sorption into activated sludge. Adsorption onto sludge may be the most important process controlling the elimination of these compounds from wastewater.



Page, D.S., C.C. Ozbal, M.E. Lanphear. *Environmental Pollution* (1996) 91:2, 237-243. Concentration of Butyltin Species in Sediments Associated with Shipyard Activity.

Tributyltin (TBT) and dibutyltin (DBT) were analyzed in sediment samples collected from intertidal locations in Portland and Boothbay Harbor, Maine (USA) in 1990 and 1992. Surface sediment TBT concentrations ranged from 24-12400 ng gm<sup>-1</sup> (dry wt basis). Sediments with the highest TBT concentrations were associated with shipyard hull washing/refinishing activities. Analysis of different layers in core samples found that butyltin concentrations decreased with depth at the Boothbay site and remained relatively constant with depth at the Portland site. Elutriate analysis showed that soluble TBT was released from a heavily contaminated sediment. The resulting TBT seawater concentration of 1400 ng liter<sup>-1</sup> was <0.03% of reported seawater solubilities of TBT and was only 0.14% of the total TBT in the sediment sample. This suggests that the TBT in the sediments analysed is in a bound matrix form, such as paint particles, that releases the biocide slowly. The results indicate that there is a potential for future release of TBT from the resuspension of fine sediments at certain locations in Maine.

TBT inputs to nearshore biological communities were associated with marinas and pleasure-boat use. Therefore ocean-going vessels and other craft greater than 25 m in length have been generally exempt from the prohibition of TBT use. Antifouling paints have been formulated with slow-release forms of TBT to minimize adverse environmental effects. The environmental degradation of dissolved TBT has been reported to proceed by successive dealkylation reactions to produce DBT and monobutyltin (MBT). TBT degrades naturally in coastal waters with a reported half-life ranging from 3-15 days depending on temperature and other natural factors. Estimates for the half-life of TBT in sediments ranges from 4 months to > 8 years depending on the nature of the sediment and the form of the TBT present. TBT contained in paint particles would be very resistant to biodegradation. This makes TBT contaminated sediments a potential source for future TBT environmental exposure. There is evidence that sediment resuspension in marinas and shipyards can release TBT to the water column with possible adverse affects on biota. TBT can also be ingested directly from contaminated sediments by deposit-feeders. Where TBT is present as TBT-containing paint residue, the release of TBT to the water column would not be governed by water solubility, but by the leaching rate of TBT from the paint matrix.

Randall, Louise and Weber, James H. *The Science of the Total Environment* (1986) 57, 191-203. Adsorptive Behavior of Butyltin Compounds Under Simulated Estuarine Conditions.

A 2<sup>3</sup> + 1 factorial design was used to study adsorption of BuSnCl<sub>3</sub>, Bu<sub>2</sub>SnCl<sub>2</sub>, and Bu<sub>3</sub>SnCl under simulated estuarine conditions. The variables included artificial seawater and its dilutions (salinity 5-35g kg<sup>-1</sup>), pH (6.2-8.2), and hydrous iron oxide concentrations (10-1000 mg l<sup>-1</sup>). Fulvic acid concentration was constant at 10 mg l<sup>-1</sup>, and initial concentration of butyltin compounds was 10 ng ml<sup>-1</sup> (as Sn). Adsorption of butyltin compounds varied from 72-100% for BuSnCl<sub>3</sub>, 0-56% for Bu<sub>2</sub>SnCl<sub>2</sub>, and 57-95% for Bu<sub>3</sub>SnCl. At the 95% confidence level all three variables were significant for BuSnCl<sub>3</sub> adsorption, pH was significant for Bu<sub>2</sub>SnCl<sub>2</sub> adsorption, and pH and salinity were significant for Bu<sub>3</sub>SnCl adsorption. Discussion includes the importance of, and reasons for, differing adsorptive behavior of the three butyltin compounds.

TBT compounds remain in the aqueous layer, adsorb onto particulates, and partition to biota, sediment or surface microlayer. If settled particulate is ingested by filter feeders or detrital feeders, there is a possibility of TBT bioaccumulating or being excreted and recycled to the aqueous phase. Studies indicate that TBT binds strongly to sediments. There is a decreased efficiency of removal as the quantity of particulate matter increases. Increased salinity also coincides with increased TBT removal. Increase in pH resulted in a decrease of TBT removal.

## **Appendix B**

### **Annotations of Research Related to Tributyltin in Wastewater**

Adelman, David, Kenneth R. Hinga, Michael E.Q. Pilson. *Environmental Science and Technology* (1990) 24, 1027-1032. Biogeochemistry of Butyltins in an Enclosed Marine Ecosystem.

Tributyltin (TBT) and its degradation products were studied by introducing radiolabeled tributyltin into a 13-m<sup>3</sup> marine enclosure (a MERL mesocosm) with near-natural water column and benthos. TBT and its degradation products were monitored for 278 days. TBT concentrations in the water column (initially  $590 \pm 20$  ng/L) decreased at a rate of  $0.20 \text{ day}^{-1}$  for 15 days and then slowed to  $0.10 \text{ day}^{-1}$ . Two-thirds of the degradation proceeded through debutylation to dibutyltin (DBT), which in turn degraded to monobutyltin (MBT) at  $\sim 0.04 \text{ day}^{-1}$ . One-third of the TBT was degraded directly to MBT. There was no evidence for degradation of MBT in the water. Another portion of the TBT removed from the water column was transported to sediments. TBT in the sediments did not appear to measurably degrade. A portion of the TBT was apparently transported rapidly to the air-water interface and then was lost from the tank.

City of Palo Alto Regional Water Quality Control Board. Clean Bay Plan, 1997.

This report is broad in its consideration of pollutants to the environment and does not focus on TBT contamination in any depth. The report outlines several sources of possible contaminants and suggests remedies as well as a course of action for all agencies involved in water quality. Tributyltin is mentioned in passing as an urban pesticide and there is little information on the subject. This report mentions the evaluation written by Dr. Nita Davidson, *Evaluation of Copper- and Tributyltin-Containing Compounds*.

Davidson, Nita A. *Evaluation of Copper- and Tributyltin-Containing Compounds*, Report Number EH-95-07 (August, 1995). California Environmental Protection Agency, Dept. of Pesticide Regulation.

This report is a result of a bill introduced into the California State Assembly (AB 3394) by Byron Sher (D, Palo Alto) that addressed the excessive discharge of copper and TBT into bays, estuaries and inland surface waters. This report establishes a high-priority program to address the sale and use of copper and TBT containing pesticides. It states the water quality objectives for TBT and the probable sources of contamination. The basis for the program is to phase out the use of TBT in order to reduce existing concentrations. The report suggests alternative uses for TBT-containing compounds, particularly those used in water towers because towers were determined to be a large source of TBT in the San Francisco Bay area. There is a reference list that focuses on monitoring results from various sites and the problems experienced by biota. The report mentions wastewater technology and the high contamination of sediment and sludge, but does not explain the procedures in detail. The focus of the report is not removing TBT from the wastewaters but reducing the concentrations over time.

de Mora, S.J., C. Stewart, D. Phillips. *Marine Pollution Bulletin* (1995) 30:1, 50-57. Sources and Rate of Degradation of Tri(n-butyl)tin in Marine Sediments Near Auckland, New Zealand.

Sediment cores were collected from marinas, a commercial wharf and a naval shipyard. TBT distribution is determined in the surface layer from cores collected along transect lines that represent shipping lanes, dredge soil dump sites, sites frequented by sport fishermen, yacht moorings and slipways. The cores were collected 1-2 years after the ban on TBT. Evidence indicates that the ban on TBT has decreased the flux of this compound to the marine environment. There is also mention of the Royal New Zealand Navy implementing a collection and treatment system for the effluent from its dry-dock at Devonport Base. Degradation kinetics were determined to be first order. Half lives ranged from 1-4 years.

de Mora, Stephen J., editor. *Tributyltin: Case Study of an Environmental Contaminant*. Cambridge University Press (Cambridge, Great Britain), 1996.

Each chapter in this book details a specific aspect of TBT contamination. Fate and transport of TBT, toxicity and degradation, industrial manufacturing, analytical techniques, and the implementation and efficacy of legislation on controlling TBT in the marine environment are addressed.

Evans, S.M., T. Leksono, P.D. McKinnell. *Marine Pollution Bulletin* (1995) 30:1, 14-21. Tributyltin Pollution: A Diminishing Problem Following Legislation Limiting the Use of TBT-Based Anti-fouling Paints.

This paper describes the improvements in biota after the ban on TBT in areas of New Zealand. Supporting evidence such as an increase in reproduction, decrease in imposex, and improvements in the health of oysters during harvest is included. Other studies are cited to support the claims; therefore, an extensive citation list is included.

Hewitt, C. Nicholas, P.J. Metcalfe, R.A. Street. *Water Research* (1991) 25:1, 91-94. A Method for the Sampling and Removal of Ionic Alkyllead Compounds from Aqueous Solution Using Ion Exchange Media.

The synthetic resin, Amberlite IR-120 in the Na<sup>+</sup> form (10 cm<sup>3</sup>), and the naturally occurring zeolite, clinoptilolite (20 cm<sup>3</sup>) have been found to quantitatively remove trimethyllead (TriML) from aqueous solutions of ionic strength up to 10<sup>-2</sup> molar NaCl. Elution by 150 cm<sup>3</sup> 2.7M NaCl removes the TriML back into solution, from where it can be extracted, derivatized with propyl Grignard reagent and analyzed by GC-AAS. TriML is stable for at least 24 h on the ion-exchange media. The method allows the sampling and determination of TriML in natural and wastewaters with a detection limit of 0.1 ng (Pb) dm<sup>-3</sup>. It may also be used for the decontamination of wastewaters. This technique may be applicable to other ionic organometallic compounds, including tributyltin.

Huggett, Robert J., Michael A. Unger, Peter F. Seligman, Aldis O. Valkirs. *Environmental Science and Technology* (1992) 26:2, 232-237. The Marine Biocide Tributyltin: Assessing and Managing the Environmental Risks.

A descriptive paper stating the history of TBT and its legislative history in Europe and the U.S. There is a small discussion on risk characterization and risk management. Like most descriptive papers, information is disseminated but few conclusions are drawn. No specific recommendations concerning the management TBT are stated. The authors do express concerns about standardization of methods for field verification, the need for improved toxicity testing, and a need for consistency to make intercomparisons easier for those who must comply with the eventual environmental statutes. The citations include several state and federal statutes and studies.

Laughlin, Roy B., Jr., Harold E. Guard, William M. Coleman, III. *Environmental Science and Technology* (1986) 20:2, 201-204. Tributyltin in Seawater: Speciation and Octanol-Water Partition Coefficient.

Analysis of chloroform extracts of tributyltin (TBT) dissolved in seawater shows that the equilibrium mixture of speciation products is composed of tributyltin chloride (TBTCl), tributyltin

hydroxide (TBTOH), the aquo complex ( $\text{TBTOH}^{2+}$ ) (as a function of pH), and a tributyltin carbonate species. The equilibrium distribution is influenced by  $[\text{Cl}^-]$ , dissolved  $\text{CO}_2$ , and pH and is easily displaced by variation within the environmental concentration range of these substances. Octanol-water partition coefficients ( $K_{\text{ow}}$ ) for tributyltin vary as a function of salinity. The lowest value, 5500, was measured in 25 ‰ and increased in higher or lower salinities to a maximum of 7000 in deionized water. The  $K_{\text{ow}}$  values reported here are substantially higher than some previous reports in the literature but are in more reasonable agreement with published bioaccumulation measurements for tributyltin assuming partitioning processes are responsible.

Lee, Richard F., Aldis O. Valkirs, Peter F. Seligman. *Environmental Science and Technology* (1989) 23:12, 1515-1518. Importance of Microalgae in the Biodegradation of Tributyltin in Estuarine Waters.

Low concentrations of tributyltin (TBT) (<5 ng/L) were found in an estuarine river along the Georgia coast. Half-lives of TBT (both radiolabeled and unlabeled) added to these waters, ranged from 3 to 13 days. Evidence suggesting that microalgae play an important role in TBT degradation in sunlit coastal waters included the following: (1) TBT degradation rates were high in light when compared to dark degradation and there was no evidence of TBT photolysis; (2) (hydroxybutyl)tins and dibutyltin were the major degradation products in the light and by cultures of diatoms and dinoflagellates, while only dibutyltin was observed in the dark; (3) TBT degradation increased in sunlight when nitrate was added. Stimulation of algal growth may be of use in enclosed aquatic areas with organotins, since dense algal cultures can rapidly degrade these organometallic compounds.

Maguire, R. James and Tkacz, Richard. *Journal of Agriculture and Food Chemistry* (1985) 33, 947-953. Degradation of the Tri-n-butyltin Species in Water and Sediment from Toronto Harbor.

Contamination of water and sediment in Toronto Harbor by the highly toxic tri-n-butyltin species ( $\text{Bu}_3\text{Sn}^+$ ) and its less toxic degradation products, the di-n-butyltin species ( $\text{Bu}_2\text{Sn}^{2+}$ ), n-butyltin species ( $\text{BuSn}^{3+}$ ), and inorganic tin, is demonstrated. At some locations the concentration of  $\text{Bu}_3\text{Sn}^+$  in water is high enough to warrant concern with regard to chronic toxicity to sensitive organisms. The  $\text{Bu}_3\text{Sn}^+$  species (i) is bound strongly to sterile Toronto Harbor sediment and the half-life of desorption is at least 10 months at 20°C, (ii) can be taken up from sediment and degraded by oligochaetes, and (iii) is degraded by a sequential debutylation pathway at 20°C in Toronto Harbor water and water-sediment mixtures with half-lives of 5 and 4 months, respectively. On the basis of this and earlier work it is concluded that the main factors limiting the persistence of the tri-n-butyltin species in aquatic ecosystems are photolysis in water and biological degradations in water and sediment, and with the temperatures and sunlight intensities prevalent in Canada, the half-life is likely to be at least a few to several months.

Maguire, R.J., P.T.S. Wong J.S. Rhamey. *Canadian Journal of Fisheries and Aquatic Sciences* (1984) 41, 537-540. Accumulation and Metabolism of Tri-n-butyltin Cation by a Green Alga, *Ankistrodesmus falcatus*.

Tributyltin pesticides are increasingly widespread, but their environmental persistence is poorly known. The accumulation and metabolism of tri-n-butyltin cation ( $\text{Bu}_3\text{Sn}^+$ ) by a green alga, *Ankistrodesmus falcatus*, was determined at 20°C over a 4-wk period; about 50% of the original  $\text{Bu}_3\text{Sn}^+$  was converted to di-n-butyltin ( $\text{Bu}_2\text{Sn}^{2+}$ ) and small quantities of butyltin ( $\text{BuSn}^{3+}$ ) and inorganic tin. An apparent algal bioconcentration factor of  $3 \times 10^4$  was estimated for  $\text{Bu}_3\text{Sn}^+$ .

Minchin, Dan, Jörg Oehlmann, Colm B. Duggan, Eberhard Stroben, Michael Keatinge. *Marine Pollution Bulletin* (1995) 30:10, 633-639. Marine TBT Antifouling Contamination in Ireland, Following Legislation in 1987.

The prevalence of imposex in dogwhelks was used as a measurement of TBT concentrations in the water column. Salmon farms, heavy shipping areas, and marinas in Ireland were sampled. TBT values were calculated based on ratios of the degree of imposex in females as compared to the standard male. The decline of imposex levels implies that the reduction of organotin levels is a positive change for the environment. However, because the ban does not extend to vessels larger than 25 m, imposex still remains and in some areas the dogwhelks are sterile or they are no longer found. There is no evidence or mention of how to control the concentrations discharged into the waters, only that reduced concentrations seem to be effective.

Müller, Markus D., Lara Renberg, Gerd Rippen. *Chemosphere* (1989) 18:9/10, 2015-2042. Tributyltin in the Environment - Sources, Fate and Determination: An Assessment of Present Status and Research Needs.

This report was prepared for the Directorate General XII of the Commission for European Community. It gives detailed conclusions and recommendations for further research and provides an extensive list of references. It is somewhat dated, however, as there is now existing research in the exact areas this report suggests. There is no specific technology mentioned other than that of sewage treatment facilities.

Sadiki, Abdel-Ilah, David T. Williams, Richard Carrier, Barry Thomas. *Chemosphere* (1996) 32:12, 2389-2398. Pilot Study on the Contamination by Organotin Compounds from PVC Materials.

Tap water from residential areas where PVC pipe had been recently installed as well as raw and treated water from water treatment plants was collected and analyzed for several organotins. The purpose of the study was to determine if organotin compounds could leach into drinking water during distribution. Organotins were not detected in either raw or treated water from samples obtained at treatment plants. Butyltin was detected in only 3 samples and all concentrations were <5 ppt. Methyltin concentrations comprised the bulk of the organotins found in tap water. The paper states the dibutyl-, monobutyl- and methyltins are the primary stabilizers used in PVC piping. There was no tributyltin detected in any samples.

Seligman, Peter F., Aldis O. Valkirs, Richard F. Lee. *Environmental Science and Technology* (1986) 20:2, 1229-1235. Degradation of Tributyltin in San Diego Bay, California, Waters.

Several experiments were carried out to determine the degradation rate of tributyltin (TBT) in microcosms containing harbor water. Unlabeled or  $^{14}\text{C}$ -labeled tributyltin was added to water samples collected from two stations in San Diego Bay, CA. Degradation rates were determined by calculating the rate of loss of the added parent TBT compound. Calculated half-lives in water collected from a yacht harbor (ambient concentration was  $0.5\ \mu\text{g}$  of TBT/L) were 6 and 7 days for light and dark treatments, respectively. Half-lives from a clean-water site ( $<0.03\ \mu\text{g}$  of TBT/L) were 9 and 19 days for light and dark treatments, respectively. The principal degradation product in all experiments was dibutyltin with lesser amounts of monobutyltin. Complete mineralization, measured by the formation of  $^{14}\text{CO}_2$ , proceeded slowly with a half-life of 50-75 days. Tributyltin at high concentrations ( $744\ \mu\text{g/L}$ ) was not degraded in sunlight, indicating that photolysis was not taking place and that biological degradation was the primary degradative process for TBT at low ambient concentrations.

Seligman, Peter F., Aldis O. Valkirs, Peter M. Stang, Richard F. Lee. *Marine Pollution Bulletin* (1988) 19:10, 531-534. Evidence for Rapid Degradation of Tributyltin in a Marina.

Die-away degradation experiments are used to determine degradation rates of TBT in a marina. Radio-labeled and non-labeled TBT was added to water collected from a marina. The water was placed in polycarbonate bottles and incubated in a tank of flowing seawater. Half lives of TBT ranged from 6-7 days. This paper advocates restricting the size of the craft eligible to use paints containing TBT as a method for managing TBT concentrations. It does not state any procedures to reduce existing concentrations to lower values.

Seligman, Peter F., J.G. Grovhoug, R.L. Fransham, B. Davidson, A.O. Valkirs. *U.S. Navy Statutory Monitoring of Tributyltin in Selected U.S. Harbors*. Technical Report 1346 (June, 1990). Naval Ocean Systems Center, San Diego, CA 92152-5000.

This report contains over 400 data points from water sampled in the Hampton Roads area of Virginia from June, 1986 - July, 1989. Sites sampled are along the James, Elizabeth and Lafayette Rivers, the Naval Station and a site designated as Hampton Roads. These data points were taken at high and low tide, at the surface as well as depth. The samples were analyzed for tributyl-, dibutyl- and monobutyl-tin. Concentrations for sediment and tissue (bivalves) are also included. However, the data sets are far less in number, 70 for sediment and 41 for tissue.



Stang, Peter M., Richard F. Lee, Peter F. Seligman. *Environmental Science and Technology*, (1992) 26:1382-1387. Evidence for Rapid, Nonbiological Degradation of Tributyltin Compound in Autoclaved and Heat-Related Fine-Grained Sediments.

Sterile, filtered seawater was utilized in experiments to determine the abiotic degradation in marine sediments. Three treatment types were established: untreated, sterile and reduced organic carbon. It was determined that TBT was rapidly degraded to MBT when sediments were exposed to dissolved TBT in the water column. Degradation occurred on the order of days where MBT was desorbed into the bottom water during this time. This abiotic process may be feasible on a larger scale. The difficulty arises if TBT is bound to another medium not easily available for degradation, such as TBT-containing paint chips. Degradation may occur on the scale of months. Initial concentration may also be a factor.

Touray, Jaquie, Laboratory Supervisor. City of Livermore Water Resources Division, California, personal communication, April 15, 1997.

Ms. Jaquie Touray spoke of high concentrations of TBT at the Livermore Water Resources Plant. This is a unique situation because the plant is inland and has no input from coastal waters. At the time of our conversation, the source of contamination had not been determined. This plant monitors both influent and effluent for TBT. The lag time between influent and effluent sampling makes it difficult to determine the efficiency of TBT removal, however. Concentrations of TBT in their effluent range from 2 ppt to 1800 ppt. The influent range is from 19 ppt - 4000 ppt.

USEPA, Office of Research and Development. *Ambient Aquatic Life Water Quality Criteria for Tributyltin* (822/R-91-100), 1991.

This report outlines the uses of TBT and references numerous studies conducted on the toxicity, chemistry, and environmental hazards of TBT. There are several tables listing various species, the chronic and acute toxicity values if available, and the reference to the particular study cited. This document does not address the issue of how to remove TBT from the water and sediments other than to reduce the concentration of the contaminant by restricting its use in the future.

Valkirs, Aldis O, Brad Davidson, Lora L. Kear, Roy L. Fransham. *Marine Environmental Research* (1991), 32:151-167. Long Term Monitoring of Tributyltin in San Diego Bay California.

TBT concentrations were monitored in the water column, sediment and in tissue. The water column determinations show a marked decrease in TBT concentrations after the limited use of TBT containing paints was implemented as did the results from tissue analysis. Sediment concentrations did not evince this trend manifested by the other two parameters. Adsorption and slow release rate are hypothesized to be behind this.

## **Appendix C**

### **Personal Communications**

Aldrich Technical Service. April 10, 1997.

Bloom, Jill. USEPA Pesticides Division. April 10, 1997.

Child, Ron. California Products, Corp. May 19, 1997.

Clancy, Sean. Witco Corp. May 20, 1997.

Clesceri, Lenore, Dr. Rensselaer Polytechnic Institute. April 11, 1997.

Cole, Rhonda, plant manager. Vikon Chemical Co., Inc. May 21, 1997.

Davidson, Nita, Dr. State of California, Department of Pesticide Regulation, April 29, 1997.

Dunst, Russ. Wisconsin DEQ. April 10, 1997.

Forbes, Paul. Garratt-Callahan Co. April 29, 1997.

Guglielmo, Andy. Flexabar Corp. May 20, 1997.

Huang, Judy. California Water Quality Board. April 11, 1997.

Huggins, Cindy. Diall Chemical Company, Inc. May 20, 1997.

Hurt, David. CH2O International. April 28, 1997.

Jenkins, Barry. Benjamin Moore and Co. May 19, 1997.

Kelly, Mike, Vice-President. Mobile Process Technology. April 30, 1997.

Leadbeater, Alan. New Zealand Embassy, Washington, D.C. April 28, 1997.

Marchman, David, Director of Operations. Skasol. April 28, 1997.

Marchowsky, David, Director for Product Safety and Regulatory Affairs of Specialty Chemicals Division. Elf-Atochem. April 25, 1997.

Michael, Peter. San Diego Regional Water Control Board. May 2, 1997.

Miller, Laura. B.F. Goodrich Co. May 19, 1997.

Mossaad, George. Huls America, Inc. April 29, 1997.

Pliodzinskas, Al. Hempel Coatings, Inc. May 20, 1997.

Richard, Nancy. California EPA. April 11, 1997.

Robertson, Charles. Ameron Coatings. April 29, 1997.

Rudlof, Bill. Troy Corporation. April 28, 1997.

Sabin, Doug. Louisiana DEQ. April 10, 1997.

Seligman, Peter. Naval Oceans System Center, San Diego. April 18, 1997.

Spectrum Chemical. April 23, 1997.

Thedaker, Kent. NuTech Enterprises. April 29, 1997.

Touray, Jaqcue. City of Livermore Water Resources Division, California. April 15, 1997.

Wilkins, Irene. Agriculture Division of Canada. April 30, 1997.

## **Appendix D**

### **Questionnaire Responses**

### **List of Respondents and Affiliation**

<b>Name</b>	<b>Company/Affiliation</b>	<b>Location</b>
Ron Miller	National Steel & Shipbuilding Co.	San Diego, CA
Pat Killeen	Halter Marine Group Inc.,	Gulfport, MS
Dr. Gisela Holm	Swedish Environmental Research Institute	Stockholm, Sweden
Kent Thedaker	NuTech Enterprises	Oceanside, CA
Dr. Victor Axiak	University of Malta Department of Biology	Malta
Dr. G.M. Gadd	University of Dundee Department of Biology	Dundee Tayside, UK
David Marchowsky	Elf Atochem North America	Philadelphia, PA
Dr. W.J. Langston	Plymouth Marine Laboratory	Citadel Hill Plymouth, UK
Dr. Ian M. Davies	Dept. of Agriculture & Fisheries for Scotland	Marine Laboratory Aberdeen, UK
Dr. Terry Wade	Texas A&M University Dept. of Oceanography	College Station, TX
Dr. Cheryl Krone	NOAA - Northwest Fisheries Center	Seattle, WA
Richard Gomez	ITSEnvironmental Laboratories	Colchester, VT
Thomas Beacham	NORSHIPCO	Norfolk, VA
Algimantas Pliodzinskas	Hempel Coatings [USA], Inc.	Houston, TX
Al Rainsberger	Todd Shipyard	Seattle, WA
Carol Weiss		UK
Dr. A.A. Karande	Nav. Che. & Metallurg. Lab Tiger Gae	Bombay, India
Arcino Quiero, Jr.	Newport News Shipbuilding	Newport News, VA

# TRIBUTYL TIN TECHNOLOGY INVESTIGATION

Responder: Ben Miller Date: 6-23-97  
Address: NASCO  
28th Harbor Drive, San Diego, CA 92186-5278  
Phone Number: (619) 544-7280 Fax Number: (619) 732-6411

Please complete and return by June 6, 1997 to the following. Responses may be by mail, phone, fax or e-mail. Any questions you have should be directed to Lisa Ramirez at (757) 683-3498.

ODU/AMRL/CASRM

Attn: Lisa Ramirez

1034 West 45th Street

Norfolk, VA 23529-0456

Fax: (757) 683-3293

E-mail: RAMIREZ@ESTUARY.AMRL.ODU.EDU

1. Have you ever been asked to monitor for Tributyltin (TBT) in water. What steps did you take to comply with this request? Yes, in water column samples. But not for shipyard process discharges.
2. What protocol do you follow for managing TBT waste in your facility? We don't use TBT paints at the shipyard unless a customer requests. A discharge of TBT can only occur when the vessel is at pier side.
3. Are you aware of any methods for reducing TBT concentrations in water? If so, what are the methods that you used/used? Please express your pre- and post-treatment TBT concentrations in ppt (parts per trillion). unknown. we have never treated waste water that contained TBT.
4. Are you aware of any legislation in your state or region, either pending or currently enacted, that limits or will limit the concentration of TBT in water or wastewater? If so, please provide brief description. Or new renewed NPDES permit will require the monitoring of TBT within shipyard discharges.
5. In your opinion, what is the most efficient way of minimizing the hazard/potential hazard that Tributyltin causes/might cause? TBT can be contained when the vessel is under repair or construction (dry docked) but not when the vessel is at pier side.

Any additional comments or suggestions you have regarding the detection, regulation, reduction, or bioavailability of TBT in water or in sediment/sludge will be helpful.

**Date sent:** Wed, 4 Jun 1997 13:09:35 -0400  
**From:** Pat Killeen <104621.2134@compuserve.com>  
**Subject:** Tributyltin technology investigation  
**To:** Lisa Ramirez <RAMIREZ@ESTUARY.AMRL.ODU.EDU>

**From:** Pat Killeen  
Group Environmental Manager  
Halter Marine Group, Inc.

**Answers only:**

- #1-** No
- #2-** Containment/Waste Analysis/Disposal
- #3-** N/A
- #4-** N/A
- #5-** Develop/use alternative products



Date sent: Thu, 5 Jun 1997 13:44:00 -0400  
From: Pat Killeen <104621.2134@compuserve.com>  
Subject: Re: Tributyltin technology investigation  
To: "Lisa M. Ramirez" <ramirez@estuary.amrl.odu.edu>

In the case of removing a coating containing TBT-The material is either contained via 'environmental screens'-with shade factor of 90% or more. These are the black mesh type that greatly reduce off-site particulate migration. Or if the vessel is on dry-dock, the screens and a temporary steel birm or wall of 12 to 18 inches is placed in areas to block any residual runoff.

When applying coatings w/TBT, we lay plastic sheeting on the ground in the area that would be currently being painted. As we move from section to section, we move the plastic. This both reduces the total amount of plastic that would need to be disposed of and eliminates ground contamination. We then profile out this material for disposal. Depending upon analysis results of course, we would dispose in conjunction with our haz. waste or non-haz.

With regards to the state of the material, after solvent distillation, the sludges are disposed of w/haz. waste and we generally composite all of the the solids (anything contaminated with the coating, i.e., paint suits, brushes, the plastic, etc) within the one profile and dispose of them as applicable.

I hope this answers any questions (I tried not to ramble on).  
Please contact me if anything else is needed.

thanks,  
pat

**From:** "Holm, Gisela" <Gisela.Holm@astra.se.astra.com>  
**To:** "ramirez@estuary.amrl.odu.edu" <ramirez@estuary.amrl.  
**Subject:** Tributyltin  
**Date sent:** Mon, 9 Jun 1997 08:53:35 +0200

Dear Ms. Ramirez,

Thank you for the letter concerning tributyltin. I just want to answer the last question in the "Tributyltin technology investigation". The answer to that one is:

The most efficient way of minimizing the hazard that tributyltin causes is to ban it. We do not need to discuss whether it is hazardous or not; it is already proved. Furthermore, 50 ppt is far above the limit of toxicity for tributyltin.

Best regards

Gisela Holm

e-mail: gisela.holm@astra.se.astra.com

## TRIBUTYL TIN TECHNOLOGY INVESTIGATION

Responder: Kent Thedaker

Date: June 6, 1997

Address: 4749 Oceanside Blvd, Ste J, Oceanside, CA 92056

Phone Number: (760) 631-0631

Fax Number: (760) 631-0636

Please complete and return by June 6, 1997 to the following. Responses may be by mail, phone, fax or e-mail. Any questions you have should be directed to Lisa Ramirez at (757) 683-3498.

ODU/AMRL/CASRM

Attn: Lisa Ramirez

1034 West 45th Street

Norfolk, VA 23529-0456

Fax: (757) 683-5293

E-mail: RAMIREZ@ESTUARY.AMRL.ODU.EDU

1. Have you ever been asked to monitor for Tributyltin (TBT) in water. What steps did you take to comply with this request?
2. What protocol do you follow for managing TBT waste in your facility?
3. Are you aware of any methods for reducing TBT concentrations in water? If so, what are the methods that you used/used? Please express your pre- and post-treatment TBT concentrations in ppt (parts per trillion).  
*We have had some success with organometallics by using a biodegradable ~~quaternary~~ quaternary surfactant. We have not evaluated with TBT at this time*
4. Are you aware of any legislation in your state or region, either pending or currently enacted, that limits or will limit the concentration of TBT in water or wastewater? If so, please provide brief description.
5. In your opinion, what is the most efficient way of minimizing the hazard/potential hazard that Tributyltin causes/might cause?

Any additional comments or suggestions you have regarding the detection, regulation, reduction, or bioavailability of TBT in water or in sediment/sludge will be helpful.

# TRIBUTYLTIN TECHNOLOGY INVESTIGATION

Responder: VICTOR AXIAK

Date: 10 June 1997

Address: Department of Biology, University of Malta  
Misra, MALTA

Phone Number: ( ) 00356 342488

Fax Number: ( ) 00356 312110

Please complete and return by June 13, 1997. Responses may be by mail, phone, fax or e-mail. Any questions you have should be directed to Lisa Ramirez at (757) 683-3498. Respond to:

ODU/AMRL/CASRM

Attn: Lisa Ramirez

1034 West 45th Street

Norfolk, VA 23529-0456

Fax: (757) 683-5293

E-mail: RAMIREZ@ESTUARY.AMRL.ODU.EDU

1. Have you ever been asked to monitor for Tributyltin (TBT) in water. What steps did you take to comply with this request?  

YES - Used chemical analysis as well as impose as a biomarker of TBT - for TBT in local coastal waters
2. What protocol do you follow for managing TBT waste in your facility?  

None - at present.
3. Are you aware of any methods for reducing TBT concentrations in water? If so, what are the methods that you used/used? Please express your pre- and post-treatment TBT concentrations in ppt (parts per trillion).  

Experimental methods based on physical adsorption to organic phases - have been proposed in UK. (Milno - University of Sunderland)
4. Are you aware of any legislation in your state or region, either pending or currently enacted, that limits or will limit the concentration of TBT in water or wastewater? If so, please provide brief description.  

No.
5. In your opinion, what is the most efficient way of minimizing the hazard/potential hazard that Tributyltin causes/might cause?

Any additional comments or suggestions you have regarding the detection, regulation, reduction, or bioavailability of TBT in water or in sediment/sludge will be helpful.

A Conference on this aspect of TBT has been held in Malta.  
Proceedings still to be published.

# TRIBUTYLTIN TECHNOLOGY INVESTIGATION

Responder: PROF G M GADD

Date: 3 JUNE 1997

Address: DEPT BIOLOGICAL SCIENCES

UNIVERSITY OF DUNDEE, DUNDEE, DD1 4HN

Phone Number: (44) 1382 344266

Fax Number: (44) 1382 344275

Please complete and return by June 13, 1997. Responses may be by mail, phone, fax or e-mail. Any questions you have should be directed to Lisa Ramirez at (757) 683-3498. Respond to:

ODU/AMRL/CASRM

Attn: Lisa Ramirez

1034 West 45th Street

Norfolk, VA 23529-0456

Fax: (757) 683-5293

E-mail: RAMIREZ@ESTUARY.AMRL.ODU.EDU

1. Have you ever been asked to monitor for Tributyltin (TBT) in water. What steps did you take to comply with this request?  
NO
  2. What protocol do you follow for managing TBT waste in your facility?  
ANY EXCESS WASTE ROUTED THROUGH UNIVERSITY SAFETY OFFICE
  3. Are you aware of any methods for reducing TBT concentrations in water? If so, what are the methods that you used/used? Please express your pre- and post-treatment TBT concentrations in ppt (parts per trillion).  
WE HAVE WORKED ON MICROBIAL TREATMENT METHODS, E BIODEGRADATION AND BIOSORPTION. CANNOT GIVE TREATMENT LEVELS (PRE- & POST-) AS ALL PROCESSES DEPENDENT ON BIOMAS
  4. Are you aware of any legislation in your state or region, either pending or currently FORM, enacted, that limits or will limit the concentration of TBT in water or wastewater? If so, ENVIR FAC  
please provide brief description.  
UNAWARE BUT UNDOUBTEDLY EXISTS  
etc, A  
CAN  
MANIF
  5. In your opinion, what is the most efficient way of minimizing the hazard/potential hazard that Tributyltin causes/might cause?  
THE MOST EFFICIENT WAY IS OBVIOUSLY TO PREVENT ITS USE. MICROBIAL TREATMENT TECHNOLOGIES WARRANT FURTHER EXPLORATION.
- Any additional comments or suggestions you have regarding the detection, regulation, reduction, or bioavailability of TBT in water or in sediment/sludge will be helpful.

# TRIBUTYL TIN TECHNOLOGY INVESTIGATION

Responder: David G. Marchewsky

Date: 06/03/97

Address: Elf Atochem North America, Inc.

2000 Market Street, Philadelphia, PA 19103-3222

Phone Number: (215) 419-7917

Fax Number: (215) 419-5265

Please complete and return by June 6, 1997 to the following. Responses may be by mail, phone, fax or e-mail. Any questions you have should be directed to Lisa Ramirez at (757) 683-3498

ODU/AMRL/CASRM

Attn: Lisa Ramirez

1034 West 45th Street

Norfolk, VA 23529-0456

Fax: (757) 683-5293

E-mail: [RAMIREZ@ESTUARY.AMRL.ODU.EDU](mailto:RAMIREZ@ESTUARY.AMRL.ODU.EDU)

1. Have you ever been asked to monitor for Tributyltin (TBT) in water. What steps did you take to comply with this request?

We are a prime manufacturer of TBT compounds.

2. What protocol do you follow for managing TBT waste in your facility?

Incineration to a tin recovery unit.

3. Are you aware of any methods for reducing TBT concentrations in water? If so, what are the methods that you used/used? Please express your pre- and post-treatment TBT concentrations in ppt (parts per trillion).

See #2 above.

4. Are you aware of any legislation in your state or region, either pending or currently enacted, that limits or will limit the concentration of TBT in water or wastewater? If so, please provide brief description.

No

5. In your opinion, what is the most efficient way of minimizing the hazard/potential hazard that Tributyltin causes/might cause?

Please clarify "hazard/potential"

Any additional comments or suggestions you have regarding the detection, regulation, reduction, or bioavailability of TBT in water or in sediment/sludge will be helpful.

Please add my name to your mailing list regarding issues and outcome of the ODU/AMRL/CASRM.

# TRIBUTYLTIN TECHNOLOGY INVESTIGATION

Responder: J Langston Date: 1/6/97  
Address: Plymouth Marine Laboratory  
Citadel Hill Plymouth UK.  
Phone Number: +1752 ( ) 633285 Fax Number: ( )

Please complete and return by June 13, 1997. Responses may be by mail, phone, fax or e-mail. Any questions you have should be directed to Lisa Ramirez at (757) 683-3498. Respond to:

ODU/AMRL/CASRM

Attn: Lisa Ramirez

1034 West 45th Street

Norfolk, VA 23529-0456

Fax: (757) 683-5293

E-mail: RAMIREZ@ESTUARY.AMRL.ODU.EDU

1. Have you ever been asked to monitor for Tributyltin (TBT) in water. What steps did you take to comply with this request?  
Mainly in a research context: we are an  
academic Research Institute not an industrial co
2. What protocol do you follow for managing TBT waste in your facility?  
See above
3. Are you aware of any methods for reducing TBT concentrations in water? If so, what are the methods that you used/used? Please express your pre- and post-treatment TBT concentrations in ppt (parts per trillion).  
Dockyards in UK are being pressed to contain  
wastes, not discharge to water (see UK DoE
4. Are you aware of any legislation in your state or region, either pending or currently enacted, that limits or will limit the concentration of TBT in water or wastewater? If so, please provide brief description.  
UK EQS =  $2\text{ng l}^{-1}$  in environment  
(Ref DoE
5. In your opinion, what is the most efficient way of minimizing the hazard/potential hazard that Tributyltin causes/might cause?  
Strict containment procedures

Any additional comments or suggestions you have regarding the detection, regulation, reduction, or bioavailability of TBT in water or in sediment/sludge will be helpful.

## TRIBUTYLTIN TECHNOLOGY INVESTIGATION

Responder: Dr. IAN M. DAVIES

Date: 5.6.97

Address: FRS MARINE LABORATORY  
VICTORIA ROAD, ABERDEEN, UK.

Phone Number: (+44) 1224 876544

Fax Number: (+44) 1224 295511

Please complete and return by June 13, 1997. Responses may be by mail, phone, fax or e-mail. Any questions you have should be directed to Lisa Ramirez at (757) 683-3498. Respond to:

ODU/AMRL/CASRM

Attn: Lisa Ramirez

1034 West 45th Street

Norfolk, VA 23529-0456

Fax: (757) 683-5293

E-mail: RAMIREZ@ESTUARY.AMRL.ODU.EDU

1. Have you ever been asked to monitor for Tributyltin (TBT) in water. What steps did you take to comply with this request?

*Developed an analytical method for TBT in water...*

2. What protocol do you follow for managing TBT waste in your facility?

*We are a research organization, not a ship maintenance facility.*

3. Are you aware of any methods for reducing TBT concentrations in water? If so, what are the methods that you used/used? Please express your pre- and post-treatment TBT concentrations in ppt (parts per trillion).

4. Are you aware of any legislation in your state or region, either pending or currently enacted, that limits or will limit the concentration of TBT in water or wastewater? If so, please provide brief description.

*UK. Has an EQS of about 3 ng/L*

5. In your opinion, what is the most efficient way of minimizing the hazard/potential hazard that Tributyltin causes/might cause?

*Prevent discharge to the environment.*

*Use closed systems in dry docks.*

*Develop less toxic alternatives.*

Any additional comments or suggestions you have regarding the detection, regulation, reduction, or bioavailability of TBT in water or in sediment/sludge will be helpful.



# TRIBUTYLTIN TECHNOLOGY INVESTIGATION

Responder: Dr. Terry L. Woot

Date: 5/30/97

Address: 833 Graham Rd, GERM

College Station, TX 77845

Phone Number: (409) 862-2323

Fax Number: (409) 862-2361

Please complete and return by June 6, 1997 to the following. Responses may be by mail, phone, fax or e-mail. Any questions you have should be directed to Lisa Ramirez at (757) 683-3498.

ODU/AMRL/CASRM

Attn: Lisa Ramirez

1034 West 45th Street

Norfolk, VA 23529-0456

Fax: (757) 683-5293

E-mail: RAMIREZ@ESTUARY.AMRL.ODU.EDU

1. Have you ever been asked to monitor for Tributyltin (TBT) in water. What steps did you take to comply with this request? *We analyze TBT in water for selected clients for their monitoring needs*
2. What protocol do you follow for managing TBT waste in your facility?
3. Are you aware of any methods for reducing TBT concentrations in water? If so, what are the methods that you used/used? Please express your pre- and post-treatment TBT concentrations in ppt (parts per trillion).
4. Are you aware of any legislation in your state or region, either pending or currently enacted, that limits or will limit the concentration of TBT in water or wastewater? If so, please provide brief description.
5. In your opinion, what is the most efficient way of minimizing the hazard/potential hazard that Tributyltin causes/might cause?

Any additional comments or suggestions you have regarding the detection, regulation, reduction, or bioavailability of TBT in water or in sediment/sludge will be helpful.

*See Attached Reprints 'T21' Ray I Smith  
Handy 43*

Ramirez

TRIBUTYLtin TECHNOLOGY INVESTIGATION

NOAA - Northwest Fish. Cent.  
Responder: Dr. Cheryl Krone Date: 6-3-97  
Address: 2725 Montlake Blvd E.  
Seattle WA 98112  
Phone Number: (206) 860-3309 Fax Number: (206) 860-3335

Please complete and return by June 6, 1997 to the following. Responses may be by mail, phone, fax or e-mail. Any questions you have should be directed to Lisa Ramirez at (757) 683-3498.

ODU/AMRL/CASRM

Attn: Lisa Ramirez

1034 West 45th Street

Norfolk, VA 23529-0456

Fax: (757) 683-5293

E-mail: RAMIREZ@ESTUARY.AMRL.ODU.EDU

1. Have you ever been asked to monitor for Tributyltin (TBT) in water. What steps did you take to comply with this request? Yes; however the monitoring was internal research projects. We modified our tissue sediment TBT methods to analyze for TBT in water.
2. What protocol do you follow for managing TBT waste in your facility?  
As a research lab we don't have a traditional TBT waste stream. A commercial hazardous waste disposal contractor picks up TBT and other chemical waste for disposal.
3. Are you aware of any methods for reducing TBT concentrations in water? If so, what are the methods that you used/used? Please express your pre- and post-treatment TBT concentrations in ppt (parts per trillion).  
NO
4. Are you aware of any legislation in your state or region, either pending or currently enacted, that limits or will limit the concentration of TBT in water or wastewater? If so, please provide brief description.  
NO
5. In your opinion, what is the most efficient way of minimizing the hazard/potential hazard that Tributyltin causes/might cause?  
minimize the use of TBT when possible.

Any additional comments or suggestions you have regarding the detection, regulation, reduction, or bioavailability of TBT in water or in sediment/sludge will be helpful.

# TRIBUTYLtin TECHNOLOGY INVESTIGATION

Responder: Richard Gomez Date: 6/6/97  
Address: ITS Environmental Laboratories  
55 South Park Drive  
Colchester, VT 05446  
Phone Number: (802) 655-1203 Fax Number: (802) 655-1248

Please complete and return by June 6, 1997 to the following. Responses may be by mail, phone, fax or e-mail. Any questions you have should be directed to Lisa Ramirez at (757) 583-3498.

ODU/AMRL/CASRM

Attn: Lisa Ramirez

1034 West 45th Street

Norfolk, VA 23529-0456

Fax: (757) 683-5293

E-mail: RAMIREZ@ESTUARY.AMRL.ODU.EDU

1. Have you ever been asked to monitor for Tributyltin (TBT) in water. What steps did you take to comply with this request? *Yes we have. As a laboratory, we have analyzed for TBT in water, sediments and tissues at all US Navy installations. The work was performed for the Navy's consulting engineering firm contracted for the environmental work.*
2. What protocol do you follow for managing TBT waste in your facility? *Our laboratory TBT waste is quite small and limited to calibration standards and small sample quantities which are properly disposed of by a reputable waste handler.*
3. Are you aware of any methods for reducing TBT concentrations in water? If so, what are the methods that you used/used? Please express your pre- and post-treatment TBT concentrations in ppt (parts per trillion). *NO. We are an environmental laboratory and not a consulting engineering firm.*
4. Are you aware of any legislation in your state or region, either pending or currently enacted, that limits or will limit the concentration of TBT in water or wastewater? If so, please provide brief description. *I am not aware of any pending legislation concerning TBT limits in the St. of VT. If I come across something I'll forward it to you.*
5. In your opinion, what is the most efficient way of minimizing the hazard/potential hazard that Tributyltin causes/might cause? *Obviously, don't use an antifouling paint that contains Tributyltin.*

Any additional comments or suggestions you have regarding the detection, regulation, reduction, or bioavailability of TBT in water or in sediment/sludge will be helpful.

Post-It FAX NO: 1011	5/29/97 pages
To: LISA RAMIREZ	From: T.L. BEACHAM
Co./Dept: ODU/AMRL/CASRM	Cu:
Phone #: 683-5293	Phone #:

# TRIBUTYL TIN TECHNOLOGY INVESTIGATION

Responder: Thomas Beacham Date: 5-29-97  
 Address: 250 W. Bentley Ave (Norfolk)  
Norfolk, VA 23501  
 Phone Number: (757) 494-4063 Fax Number: (757) 4088

Please complete and return by June 6, 1997 to the following. Responses may be by mail, phone, fax or e-mail. Any questions you have should be directed to Lisa Ramirez at (757) 683-3498.

ODU/AMRL/CASRM

Attn: Lisa Ramirez

1034 West 45th Street

Norfolk, VA 23529-0446

Fax: (757) 683-5293

E-mail: RAMIREZ@ESTUARY.AMRL.ODU.EDU

- Have you ever been asked to monitor for Tributyltin (TBT) in water. What steps did you take to comply with this request? Yes, Virginia VDES permit.  
 ① Advise state police to application for permit.  
 ② Sample for TBT per permit requirement.
- What protocol do you follow for managing TBT waste in your facility?  
We use BMPs as required by permit.
- Are you aware of any methods for reducing TBT concentrations in water? If so, what are the methods that you used/used? Please express your pre- and post-treatment TBT concentrations in ppt (parts per trillion). We have recently used  
RAF → carbon bed technology for TBT wastewater  
pre treatment = > 190,000 ppt  
post = 200 ppt.
- Are you aware of any legislation in your state or region, either pending or currently enacted, that limits or will limit the concentration of TBT in water or wastewater? If so, please provide brief description. Virginia Shipyard are currently  
regulated at 50 ppt TBT via permit.
- In your opinion, what is the most efficient way of minimizing the hazard/potential hazard that Tributyltin causes/might cause? ① Not use water to wash vessel.  
NOTE: This is not possible as this operation must  
be done to remove salts.  
 ② collect & treat.

Any additional comments or suggestions you have regarding the detection, regulation, reduction, or bioavailability of TBT in water or in sediment/sludge will be helpful.

TBT Testing procedures are inadequate for  
ppt determination, 46

# TRIBUTYL TIN TECHNOLOGY INVESTIGATION

Responder: AL RAMSBERGER  
TODD SHIPYARO

Date: 6/2/97

Address: P.O. Box 3806  
SEATTLE, WA 98124

Phone Number: (206) 623 1635

Fax Number: (206) 442-8519

Please complete and return by June 6, 1997 to the following. Responses may be by mail, phone, fax or e-mail. Any questions you have should be directed to Lisa Ramirez at (757) 683-3498.

ODU/AMRL/CASRM

Attn: Lisa Ramirez

1034 West 45th Street

Norfolk, VA 23529-0456

Fax: (757) 683-5293

E-mail: RAMIREZ@ESTUARY.AMRL.ODU.EDU

- Have you ever been asked to monitor for Tributyltin (TBT) in water. What steps did you take to comply with this request?  
AS PART OF OUR NPDES PERMIT WE NOW ARE REQUIRED TO SAMPLE. A GRAB SAMPLE IS TAKEN AS THE DRYDOCK IS FLOODED.
- What protocol do you follow for managing TBT waste in your facility?  
US DEPT OF AGRICULTURE APPLICATION AND CERTIFICATION RCRA WASTE DISPOSAL
- Are you aware of any methods for reducing TBT concentrations in water? If so, what are the methods that you used/used? Please express your pre- and post-treatment TBT concentrations in ppt (parts per trillion).  
NO
- Are you aware of any legislation in your state or region, either pending or currently enacted, that limits or will limit the concentration of TBT in water or wastewater? If so, please provide brief description.  
NO
- In your opinion, what is the most efficient way of minimizing the hazard/potential hazard that Tributyltin causes/might cause?  
BMP'S

Any additional comments or suggestions you have regarding the detection, regulation, reduction or bioavailability of TBT in water or in sediment/sludge will be helpful.

**From:** "Carol Weiss" <C.A.Weiss@newcastle.ac.uk>  
**To:** RAMIREZ@ESTUARY.AMRL.ODU.EDU  
**Date sent:** Wed, 11 Jun 1997 10:05:05 +0000  
**Subject:** Tributyltin Technology Investigation  
**Send reply to:** C.A.Weiss@newcastle.ac.uk  
**Priority:** normal

Dear Ms Ramirez,

Here are the answers to the survey you conducted. I have answered the ones that are applicable.

1. Have you ever been asked to monitor for Tributyltin (TBT) in water. What steps did you take to comply with this request?

- We have been monitoring imposex in gastropods as a biological indicator of TBT contamination since 1986. Some of the work has been funded by organotin producers and the paint industry. We have also worked in collaboration with the Environment Agency.

3. Are you aware of any methods for reducing TBT concentrations in water? If so, what are the methods that you used? Please express you pre- and post-treatment TBT concentrations in ppt (parts per trillion).

- The Ecology Centre at Sunderland University (UK) has been working on waste water treatment techniques to reduce TBT (contact Dr. Abel).

5. In your opinion, what is the most efficient way of minimising the hazard/potential hazard tha Tributyltin causes/might cause?

- It would be useful to have proper cost / benefit analysis of the use of TBT assessment of the impact of TBT on marine ecosystems. There is a great deal of misinformation in the system. For example, two of the gastropods, which are reputed to be on the verge of extinction due to TBT pollution are in fact abundant along our own coasts and elsewhere in the North Sea.

I hope these are of some use to you.

Yours sincerely,

Damien Smith

(Secretary)

# 20/6/97 1 -> 12 12 1 12

From: Algimantas Pliodzinskas, HSE Coordinator HEMPEL COATINGS [USA] INC.  
Questions? Call 713-672-6641 6901 Cavalcade  
Fax 713-672-0616 Houston, Texas 77028  
To: Lisa Ramirez cc: M.Bentkjaer, TSD  
Company: Applied Marine Research Labs (757) 683-5293, (757) 683-5293  
Address: Norfolk, VA  
Date: May 21, 1997  
Time: 9:25 AM Pages: (including this one)

---

Re: Your telephone request of 20 May for information regarding how waste TBT containing materials are handled.

Dear Ms. Ramirez:

With respect to the above topic, Hempel (USA) handles the material such that very little, if any, TBT containing material is present as waste. Containers of paint raw materials which contain TBT fully emptied into the particular batch for which they are destined. Hempel buys no TBT containing material in bulk. All such material is purchased in either 5 gallon pails or 55 gallon drums.

Drums are RCRA emptied prior to being sent to drum reconditioners. Pails and drums which are not RCRA empty [or cannot be made so] are crushed and sent to a hazardous waste landfill. Any residue which cannot be utilized in paint product is sent for disposal through fuel blending for cement kilns. All TBT containing paint products or raw materials are in a combustible form suitable for fuels blending.

Organotins are by definition pesticides and are to be disposed of in accordance with federal, state and local regulations. RCRA regulations do not specifically list Tin or TBTs as specific hazardous wastes. There is no TCLP or EP Toxicity methodology associated with this type product. Recommendations for pesticide disposal usually refer to incineration as the most effective means.

#### **WASTEWATER**

Your telephone questions actually relate to the handling of wastewaters which contain TBT. Hempel (USA) has no wastewater which contains TBT.



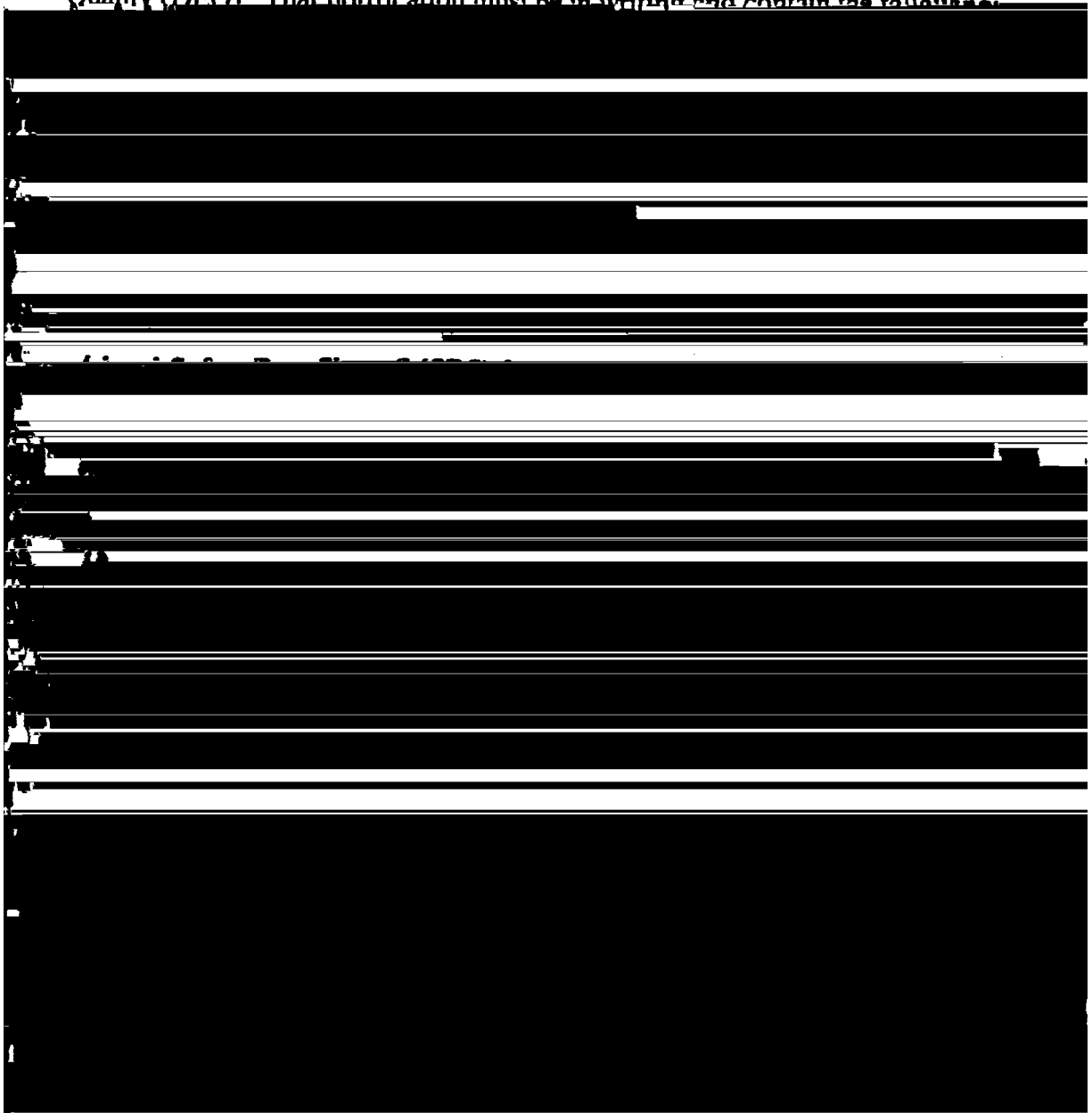
# TRIBUTYLTIN TECHNOLOGY INVESTIGATION

Responder: Arcino Quiero, Jr. (Newport News Shipbuilding) Date: June 9, 1997  
Address: 4101 Washington Avenue  
Newport News, VA 23607-2770  
Phone Number: (757) 380-7035 Fax Number: (757) 688-6007

1. Have you ever been asked to monitor for Tributyltin (TBT) in water. What steps did you take to comply with this request?

Yes, we as required to monitor for TBT as outlined by our VPDES permit.

Prior to either applying and/or removing paints and/or other hull coating materials that contain TBT we are required to notify to the Department of Environmental Quality (DEQ). That notification must be in writing and contain the following:



3. **Are you aware of any method for reducing TBT concentrations in water? If so, what are the methods that you use and/or used? Please express your pre- and post-treatment TBT concentrations in ppt (parts per trillion).**

U. S. Filter conducted a feasibility study for NNS, with guidance from Rohm & Hass and the Virginia Institute of Marine Sciences, to find a system that would remove TBT and copper from our effluent. The resins used worked relatively well for copper, but due to facility and cost limitation (\$2 Million per dock), NNS was not able to continue with this approach.

4. **Are you aware of any legislation in your state or region, either pending or currently enacted, that limits or will limits the concentration of TBT in water or wastewater? If so, please provide a brief description.**

We are required by our VPDES permit to submit to the DEQ quarterly progress reports and achieve compliance with final limits, 50 ppt, within four years from the effective date of our permit, June 4, 2000.

5. **In your opinion, what is the most efficient way of minimizing the hazard and/or potential hazard the TBT causes/might cause?**

The question that needs to be asked is "are we all playing on a level field." If we had all the answers for controlling TBT and the rest of the world is not required to play by those same rules it really does not matter.

## **Appendix E**

### **U.S. Patent Search Results**

## 3531463: Enrichments and/or Separation of an Organic Compound by Adsorption Process

**Inventors:** Richard L. Gustafson., Horsham, PA

**Abstract:** Disclosed herein is a process of separating from an aqueous medium water-soluble substance having hydrophobic and hydrophilic portions in their molecules. The process involves contacting the aqueous medium with particles of non-ionogenic, macroreticular water-insoluble cross-linked polymer of polymerizable ethylenically unsaturated molecules comprising about 2 to 100 weight percent of at least one polyvinylbenzene monomer selected from the group consisting of divinylbenzene, trivinylbenzene, alkyldivinylbenzenes having from 1 to 4 alkyl groups of 1 to 2 carbon atoms substituted in the benzene nucleus and alkyltrivinylbenzenes having from 1 to 3 alkyl groups of 1 to 2 carbon atoms substituted in the benzene nucleus.

## 3853758: Separation of Waste Dyestuffs by Adsorption Process

**Inventors:** Hurwitz; Marvin J., Elkins Park, PA  
Kennedy; David C., Melvern, PA  
Kollman; Carl J., Cherry Hill, NJ

**Abstract:** Effluents from dye manufacturing and dyeing operations which contain waste dyestuffs are decolorized and their oxygen demand substantially reduced by passing at least a major part of the effluent through a bed of essentially non-ionogenic, macroreticular, water-insoluble, cross-linked polymeric adsorbent resin followed by contacting the partially decolorized effluent with a weak acid and/or aliphatic weak base ion exchange resin.

## 4007116: Process for the Purification of Waste Waters with Activated Carbon

**Inventors:** Gappa; Gunther, Gelsenkirchen-Buer, Federal Republic of Germany  
Juntgen; Harald, Essen, Federal Republic of Germany  
Klein; Jurgen, Essen, Federal Republic of Germany  
Reichenberger; Jurgen, Essen, Federal Republic of Germany

**Abstract:** A process for the purification of waste water containing dissolved organic carbon contaminants which comprises A. passing the waste water upwardly through a column of activated carbon particles, B. determining the total organic carbon content of the water before it enters the column and simultaneously at a location that is between 30 and 70% of the total height of the carbon particles in the column, C. continuously withdrawing the spent carbon particles from the bottom of the column at such a rate as to maintain an essentially constant preselected difference between the total organic carbon content of the water as it enters the column and at the preselected location that is between 30 and 70% of the height of the carbon particles in the column, D.

continuously introducing fresh activated carbon particles or reactivated carbon particles at the top of the column at such a rate as to compensate for those withdrawn at the bottom of the column, and E. removing the purified water at the top of the column.

## 5061374: Reverse Osmosis as Final Filter in Ultrapure Deionized Water System

**Inventors:** Lewis; Vic E., Boise, ID

**Abstract:** An improved deionized water treatment system and method that consists of using a first and second water treatment train wherein the second train improves water quality by reducing particulate and total organic carbon by means of a reverse osmosis membrane assembly. The final pure water having particulate sizes less than one micron and a total organic carbon measure of less than one part per billion.

## 5236594: Process for Removing Toxicants from Aqueous Petroleum Waste Streams

**Inventors** O'Reilly; Kirk T., El Sobrante , CA  
Suzuki; John P., Pinole, CA

**Abstract:** Specific toxicants are selectively removed from aqueous waste streams associated with the production of petroleum and petroleum products by contacting such aqueous waste streams with a non-ionic macroreticular polymeric resin having a low to intermediate surface polarity. The toxicants are a group of structurally-related organic molecules containing at least one carboxylic acid group and having a molecular weight in the range of about 200 to about 400. These molecules are toxic to certain indicator species of fish at concentrations of less than 10 part per billion.

## 5302356: Ultrapure Water Treatment System

**Inventors:**      **Shadman; Farhang F.**, Tucson, AZ  
                      **Governal; Robert A.**, Tucson, AZ

**Abstract:**      An ultrapure water treatment system is provided by the present invention. e [sic] system comprises a housing, a water supply means including a water inlet and a water outlet communicating with the housing and defining a path of travel of the water from said inlet to said outlet, irradiation means for irradiating water with 185 nm UV light positioned within the housing, and a catalytic filter positioned in the path of travel of the water. The catalytic filter comprises a non-polymeric porous material having a photoactive catalyst thereon. Exemplary photoactive catalysts include  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{WO}_3$ ,  $\text{SnO}_2$ ,  $\text{Cu}_2\text{O}$ , [sic] and  $\text{CdSe}$  [sic].

## 5376281: Water Purification System

**Inventors:**      **Safta; Eugen**, Winston-Salem NC

**Abstract:**      An apparatus for purifying water includes: a plurality of UV radiators which include a helical quartz tube through which water to be purified passes and an ultraviolet light source to irradiate water passing through the helical quartz tube to remove microbes, a plurality of filtration stages including fine, ultra-fine and micro filters, a reactor including a bed of gold, and an irradiation stage including a quartz tube through which water to be purified passes and a laser light source with a wavelength in the range of 200-300 nm to irradiate water passing through the quartz tube, whereby microbes in the water passing through the apparatus are killed and removed.

## 5399273: Oil Soluble Dispersant Additives Modified with Bis-keto/Thioketo Compounds

**Inventors:**      **Emert; Jacob**, Brooklyn, NY  
                      **Gutierrez; Antonio**, Mercerville, NJ  
                      **Lundberg; Robert D.**, Bridgewater, NJ

**Abstract:** The present invention is directed to an oil-soluble lubricating oil additive comprising at least one adduct of (A) a polyolefin of 700 to 5,000 number average molecular weight substituted nitrogen- or ester-containing ashless dispersant and (B) a bis-keto/thioketo compound.

## 5653883: Stirred Tank Biological Activated Carbon Adsorption-Desorption Process

**Inventors:**     **Newman; William A.**, Mounds View, MN 55112  
                  **Newman; Ritchey O.**, Gladwin, MI 48624

**Abstract:**     Organic contaminants are removed from water by microbial biodegradation in a stirred tank system having a powdered or granular media for biofilm support. A stirring impeller maintains the media suspension, provides a shear force to remove excess biomass from media particles and is adjustable to provide an optimal biofilm thickness.

Additional copies of this report can be obtained from the  
National Shipbuilding Research and Documentation Center:

**<http://www.nsnet.com/docctr/>**

Documentation Center  
The University of Michigan  
Transportation Research Institute  
Marine Systems Division  
2901 Baxter Road  
Ann Arbor, MI 48109-2150

Phone: 734-763-2465  
Fax: 734-936-1081  
E-mail: [Doc.Center@umich.edu](mailto:Doc.Center@umich.edu)